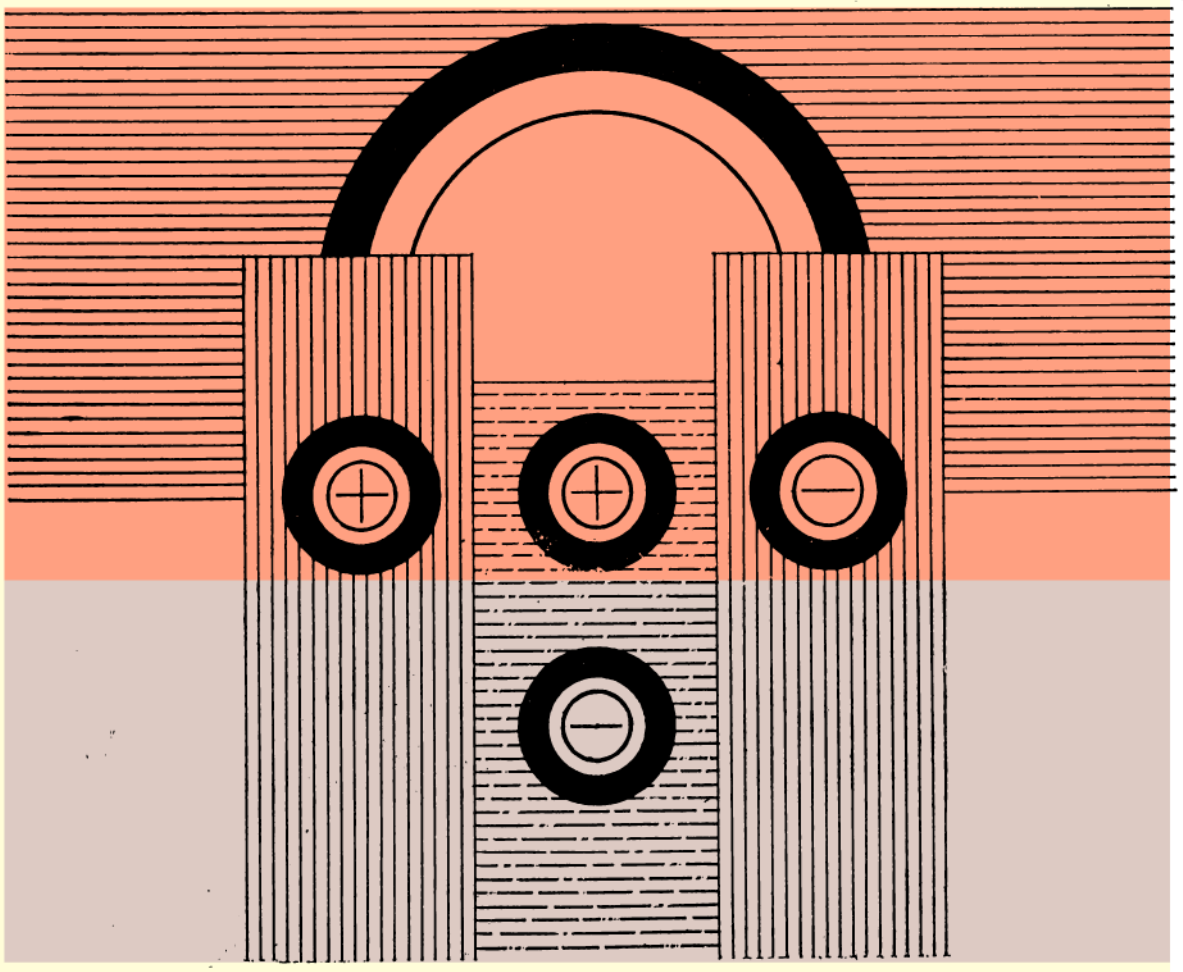
L.ANTROPOV

Theoretical Electrochemistry



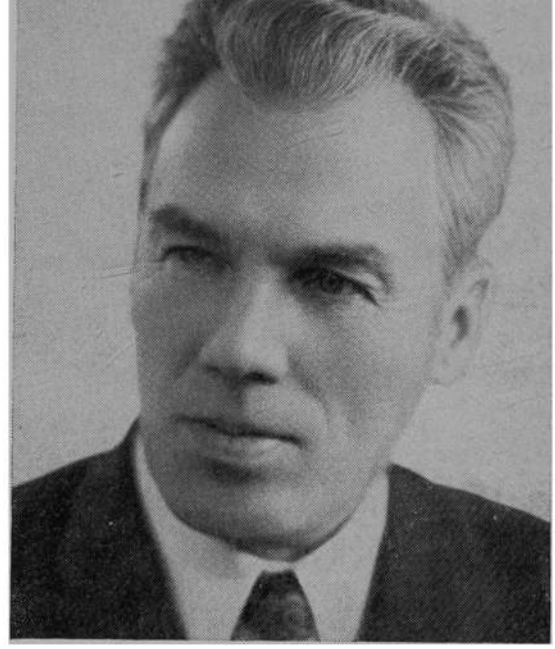
Mir Publishers

THEORETICAL ELECTROCHEMISTRY

by L. I. ANTROPOV

This textbook is designed primarily for students specializing in electrochemistry, but will be found useful by post-graduates, research workers, and engineers concerned with this field in industry. It is based on the theory of electrochemical systems originally developed by L. V. Pisarzhevsky and considers, stage by stage, the laws governing electrochemical processes and their peculiarities distinguishing these processes from ordinary chemical reactions. It discusses the equilibrium of electrolytes and the nonequilibrium phenomena occurring in them. Consideration is given to electrode equilibrium, including the structure of the double layer between the electrode and the electrolyte and perturbations caused by the passage of a current across the electrode-electrolyte interface or by deviations of the electrode potential from its equilibrium value, finally, the kinetics of the most important electrode processes is explained.

The course covers the basic elements of modern theoretical electrochemistry, presenting them in logical sequence — from equilibrium to kinetics. The material within each part and chapter is arranged so as to reflect the historical development of the field in question. The book contains much factual material in the form of tables and figures.



Professor Lev Ivanovich ANTROPOV, D. Sc., has been Head of the Department of Electrochemistry at the Kiev Polytechnic Institute since his return in 1960 from service as a UNESCO expert at the Indian Institute of Technology. He is a member of the Mendeleyev Chemical Society of the USSR, the Comité National des Dejives Tensio-Actifs de l'URSS (C.I.D.) and of the Editorial Boards of "Electrochemistry" and "Corrosion Protection" (USSR) and "Corrosion Science" (G. B.).

Prof. Antropov has published extensively in Indian, American, and British journals as well as in the USSR and has lectured in India, Japan, Poland, West Germany and the USA. He is the author of some two hundred works mainly in the field of the theory of electrochemical reduction of organic substances, of corrosion inhibition by organic compounds and electrode kinetics. He has formulated a new correlative or φ scale of potentials (also known as the reduced scale of potentials). Prof. Antropov was Vice-President of the Third International Congress on Corrosion in 1966.

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ИЗДАТЕЛЬСТВО
МИР

Л. И. АНТРОПОВ

ТЕОРЕТИЧЕСКАЯ ЭЛЕКТРОХИМИЯ

ИЗДАТЕЛЬСТВО
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L. I. ANTROPOV

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PREFACE

The rapid advance of electrochemistry and its ever closer links with and mutual enrichment of other sciences, and the continuous expansion of its various branches makes a more or less comprehensive presentation of electrochemistry an extremely difficult task.

In selecting the material and the order of presentation for this work I have been guided by the definition of electrochemistry, given by Kistyakovsky in 1912, as the science "concerned with the study of the phenomena accompanying the direct conversion of chemical energy into electrical and vice versa". This definition was taken further by Pisarzhevsky, who was the first to formulate clearly the prerequisites for mutual conversion of chemical and electrical forms of energy and introduce the concept of electrochemical systems in which this process is possible. Our presentation is based on the theory of electrochemical systems, their constituent parts and their possible states. It seems to me that these principles permit one to visualize electrochemistry as an integral whole and independent, self-contained discipline and clearly define the boundaries separating it from closely related sciences.

Much attention is paid to disclosing the physical content of electrochemical phenomena and the essence of the related theoretical conceptions. The mathematical apparatus is relatively simple, and only the general principles of electrochemical experiment are given. Experimental procedures are described in more detail only where it is necessary for the understanding of the nature of the process in question or the essence of the theoretical views concerned.

In writing this textbook I have tried to cover all the basic aspects of theoretical electrochemistry and to reflect as completely as possible the latest advances and trends in its development. I hope that this has been accomplished to some extent but though I have tried to be objective, I have probably not avoided a certain preference

for what seemed to me more correct, and particularly more important and interesting. In this connection it would seem appropriate to recall Mendeleyev's words in the preface to the fifth edition of his famous "Fundamentals of Chemistry": — 'in all objective expositions of science, there will always and inevitably be much that is subjective, bearing the stamp of the times and place... separate works, like a mirror, will reflect that which is near more clearly and strongly... although I have striven to make my book a true mirror—what is dear to me has involuntarily been reflected most sharply and illuminated more clearly, and presented, through the reflection, in all its pristine brightness'. The truth of these words has probably been felt by everyone who has tried to generalize the material of any science or branch of it.

In preparing the original Russian text for this English edition I have taken into account the advice and comments of my colleagues and pupils, to all of whom I express my sincere gratitude. Special thanks are due to my wife who contributed so generously of her time and experience in selecting the factual material, reading the entire book and making a host of suggestions to improve the clarity and rigour of the presentation. Without her constant help the book would have been impossible. Her many services above and beyond the call of duty are gratefully acknowledged.

L. I. Antropov

April 1972

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PRINCIPAL SYMBOLS

A = Maximum work; a constant in a number of equations

A_r = Real energy of ion hydration

A_{ch} = Chemical energy of ion hydration

A^- = Anion (any species)

a = Activity; mean ionic diameter; acceleration; a constant in Tafel's equation

$a_\pm$ = Mean activity of an electrolyte

a_e = Total activity of an electrolyte

B = A constant in a number of equations

B_c = Current efficiency of electrolysis

b = A constant in Tafel's equation ($2.303\ RT/\alpha F$)

b^0 = $2.303\ RT/F$

C = Capacitance (capacity)

c = Concentration (molarity); heat capacity

D = Dielectric constant

d = Density

E = Electromotive force (emf)

E^0 = Standard emf

e = Elementary charge

$\mathfrak{F}$ = Free energy (Helmholtz)

F = Faraday's constant (faraday)

f = Activity coefficient

$f_\pm$ = Mean activity coefficient

G = Free enthalpy (Gibbs free energy)

ΔG_{ch} = Chemical energy of hydration (solvation)
ΔG_r = Real energy of hydration (solvation)
G^* = Energy of ionic interaction
g = Acceleration due to gravity; internal potential; a constant in some equations
$g_{\alpha\beta}$ = Galvani potential difference (total, or absolute, potential difference between two phases α and β)
g^* = Partial energy of ionic interaction
H = Heat content (enthalpy); heat of hydration
ΔH_{ch} = Chemical heat of hydration
ΔH_r = Real heat of hydration
h = Height; a constant in the Lewis-Randall equation
I = Current; ionization energy (potential); electron affinity
i = Isotonic factor; current density
J = Ionic strength
j = Volume current density
K = Equilibrium constant; dissociation constant; solubility product
K_M = Madelung constant
K_w = Ionic product of water
K^+ = Cation (any species)
k = Coefficient of friction; velocity or rate constant; a constant in a number of equations
k = Boltzmann's constant
L = Solvent
l = Length
l_H = Thickness of the Helmholtz double layer
M = Any metal; molecular weight
M^+ = Metallic ion
m = Mass; concentration (molality)
N = Total number of particles in a system; molar fraction
N_A = Avogadro's number
n = Number of particles in unit volume; order of reaction; valency
n_h = Hydration number
P = Pressure
p = Partial pressure
$\overline{Q}$ = Thermochemical heat effect per one mole
$\overline{Q_f}$ = Heat of formation

$\overline{Q}_h$ = Heat of hydration

$\overline{Q}_L$ = Heat of solution

$\overline{Q}_S$ = Heat of solvation; heat of sublimation

q = Thermochemical heat effect per one molecule; quantity of electricity; charge

R = Universal gas constant; electrical resistance

r = Radius; distance

S = Solid body (state); entropy

T = Absolute temperature (Kelvin temperature); transport (transference) number according to Washborn

t = Centigrade temperature (Celsius temperature); time; transport (transference) number

U = Energy; internal energy; electrochemical cell voltage

U_L = Ionic energy in solution

U_V = Ionic energy in vacuum

U_S = Energy of solvation

u = Energy level; activation energy

V = Volume; dilution; vacuum; gaseous phase

v = Specific volume; velocity; absolute velocity of ions

W = Work

w = Velocity of ions

Y = Work of pulling out of ions from crystal lattice (in terms of one gram-ion)

y = Work of removing of an ion from crystal lattice (in terms of one ion); force

Z = Degree of corrosion protection

z = Number of elementary charges; charge of a particle (ion); number of electrons participating in reaction

α (alpha) = Degree of dissociation; polarizability; Brönsted's coefficient; real potential; transfer coefficient (transition factor)

β (beta) = Buffer capacity; exponent in Freundlich's isotherm

Γ (gamma) = Gibbs surface concentration (surface excess)

γ (gamma) = Viscosity; corrosion inhibition coefficient

Δ (delta) = Diffusion coefficient

δ (delta) = Thickness of diffusion layer

δ_P = Thickness of Prandtl's diffusion layer

δ_r = Thickness of reaction layer

ε (epsilon) = Electrode potential on conventional scale

ε^0 = Standard electrode potential on conventional scale

$\Delta\varepsilon$ = Electrode polarization

$\Delta\varepsilon_R$ = Depolarization

ζ (zeta) = Electrokinetic or zeta potential

η (eta) = Overvoltage (overpotential)

Θ (theta) = Degree of coverage

ϑ (theta) = Angle; contact angle

$\varkappa$ (kappa) = Specific electrical conductance, conductivity

λ (lambda) = Equivalent molar conductance; ionic conductance (mobility); heat of evaporation of water molecule

μ (mu) = Chemical potential in real system; dipole moment

$\bar{\mu}$ = Chemical potential in ideal system

μ^0 = Standard chemical potential

μ_{ech} = Electrochemical potential

ν (nu) = Number of ions formed as a result of dissociation of one molecule of electrolyte; stoichiometric number

π (pi) = Osmotic pressure

ρ (rho) = Specific resistance, resistivity; space charge density

σ (sigma) = Surface tension

τ (tau) = Time interval

τ_r = Relaxation time

φ (phi) = Electrode potential on correlative scale (zero-point scale)

χ (chi) = Quantity inverse to radius of ionic atmosphere; surface potential

Ψ (psi) = Redox kinetic potential

ψ (psi) = Electrical potential; outer potential

$\psi_{\alpha\beta}$ = Volta potential difference between phases α and β

Ω (omega) = Cross-sectional area; surface area

ω (omega) = Angular velocity; work function

INTRODUCTION

I.1. THE SUBJECT AND SCOPE OF ELECTROCHEMISTRY

Electrochemistry is concerned with study of mutual conversion of chemical and electrical forms of energy and also of the laws and regularities associated with this process. Chemical reactions are usually accompanied by absorption or evolution of heat (the heat effect of the reaction) and do not involve electrical energy. Electrochemistry deals with reactions proceeding at the expense of external electrical energy or serving as a source of this energy. Such reactions are known as *electrochemical reactions.* It is evident that, from the viewpoint of thermodynamics, electrochemical reactions are not identical to chemical reactions, and electrochemistry should therefore be regarded as an independent science.

To get a clearer understanding of electrochemistry as a science, it is necessary to consider in more detail the distinction between electrochemical and chemical reactions and to elucidate the causes due to which the energy effect of a chemical change takes the form of electrical energy in the first case and heat in the second. Let us consider, as an example, the following chemical transformation:

$$Fe^{3+} + Cu^{+} = Fe^{2+} + Cu^{2+} \qquad (I.1)$$

If this reaction takes place as a chemical process, it will have a number of specific features.

The reaction is feasible only when the reactants collide with one another. Hence, the necessity of contact between the reacting particles is the first specific feature of all chemical reactions.

At the moment of collision, when the reacting particles approach one another closely, transfer of electrons from one particle to another becomes possible. Whether this transfer of electrons actually occurs depends on the internal energy of the reacting particles and the ratio of that energy to the activation energy. The activation energy is a function of the nature of a chemical reaction; in ionic reactions

this energy, as a rule, is not great. The path travelled by an electron will be very small, this being the second characteristic feature of a chemical reaction.

Collisions may occur at any point of the reaction space, irrespective of the position the reacting particles occupy relative to one another. The electrons may therefore be transferred in any direction in space (Fig. I.1). The chaotic nature of collisions between the reacting particles and the resultant random movement of electrons

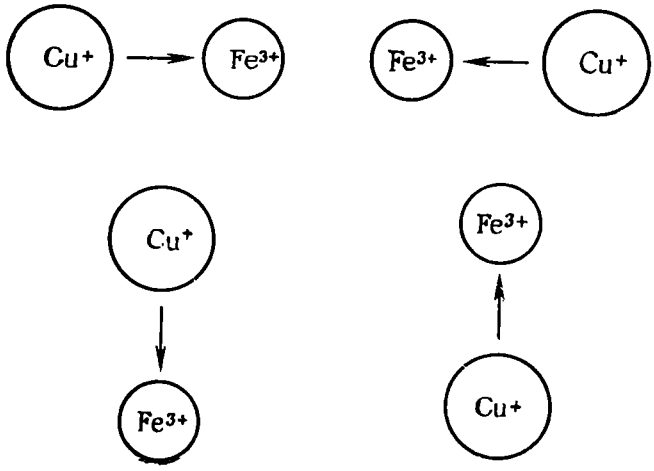

Fig. I.1. Schematic representation of electron transfers during the chemical ionic reaction $Fe^{3+} + Cu^{+} = Fe^{2+} + Cu^{2+}$

constitute the third characteristic feature of a chemical reaction.

Owing to these features of chemical processes the energy effect takes the form of heat.

For an electrochemical process to take place, the reaction conditions must be altered. The gain or loss of electrical energy is always associated with the passage of an electric current, which is a flow of electrons in one direction. The conditions of a chemical reaction must be changed so that electrons move not randomly but in a single definite direction. The use of electrical energy is possible only if the path traversed by electrons is great as compared to the size of atoms. Thus, in electrochemical reactions the electrons migrating from one participant to another must travel a sufficiently long path. The path of electron movement however cannot be long if the reacting particles are brought into contact. Therefore separation of the reactants in space is a necessary condition for an electrochemical process.

But separation of the reactants alone, that is, the absence of contact between them, would stop the chemical reaction rather than change it into an electrochemical one. Obviously, in order to effect an electrochemical reaction it is necessary to provide additional con-

ditions in which the absence of contact between the reactants would not terminate the chemical process. The electrons must be torn off from one of the participants (from copper ions in the example given above) and transferred along a single common path to the other reactant (iron ions). This can be achieved if a direct contact between the reactants is replaced by their contact with two metal plates connected by means of a metallic conductor of electricity. For the flow of electrons to be continuous an electric current must also be passed through the reaction space. This is usually realized by the reactants involved in an electrochemical reaction (provided they are in the ionized state) and/or by addition of special compounds capable of exhibiting high ionic conduction under the particular conditions.

In an electrochemical reaction, there is no direct contact between the reacting particles; instead, each of the participants is brought into contact with the electrode. In this case the reaction and the associated energy changes remain the same (no matter whether the reaction is chemical or electrochemical), but the kinetics may be different. The activation energy in an electrochemical process may differ from that in a chemical one, owing to the catalytic properties of the electrodes. Since the electrode potential may vary, the energy of activation for the electrochemical mechanism of a chemical reaction will depend not only on the nature of the reactants and the electrode, but also on the electrode potential.

From the foregoing it follows that the rate of an electrochemical reaction depends not only on the temperature, the activity of the reactants and the material of the catalyst, i.e., on the same factors that determine the rate of a chemical reaction, but also on the electrode potential. Electrochemical reactions may be defined as chemical reactions the rate of which is a function of the potential. They thus differ from chemical reactions not only from the thermodynamic (the energy effect of the process) but also from the kinetic point of view (the energy of activation).

The mutual conversion of chemical and electrical forms of energy is possible only in electrochemical systems, study of which is the field of electrochemistry.

A system in which an electrochemical process takes place is illustrated in Fig. I.2. It consists of the following parts:

(1) the reacting substances and ionized substances or substances contributing to ionization, which provide the passage of an electric current; this part of the system is an ionic conductor of electricity (conductor of the second class) and is termed the *electrolyte*;

(2) two metal plates in contact with the electrolyte, which bring about an exchange of electrons with the reactants as well as a transfer of electrons either to the external circuit (see below) or from the external circuit; these plates are known as *electrodes*;

(3) a metal conductor (conductor of the first class) connecting the electrodes and ensuring the passage of an electric current between them; it is called the *external circuit.*

When the electrolyte is a current-conducting solution of one or more substances in water or some other solvent, what we are concerned with is the electrochemistry of aqueous or nonaqueous solutions. When a molten salt or a mixture of molten salts or oxides serves as

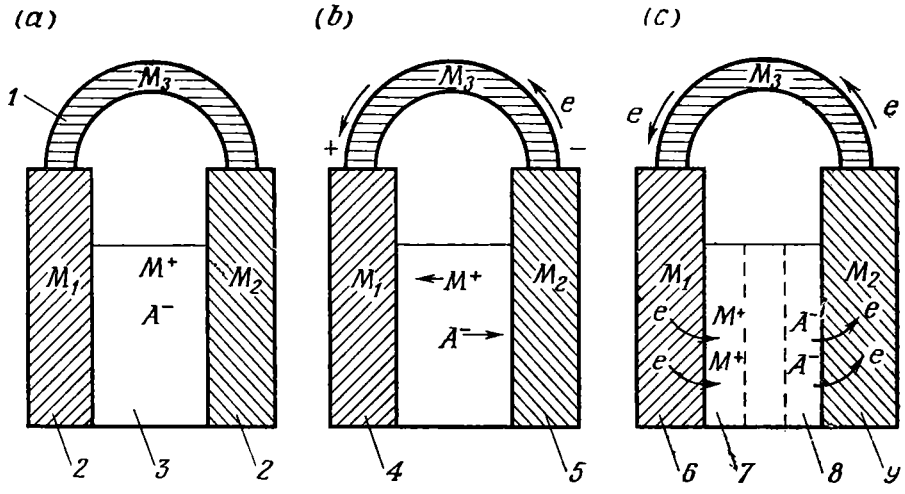

Fig. I.2. Electrochemical systems:

a—equilibrium electrochemical system; *b*—chemical source of electric current; *c*—electrolytic cell: *1*—external circuit; *2*—electrodes; *3*—electrolyte; *4*—positive electrode; *5*—negative electrode; *6*—cathode; *7*—catholyte; *8*—anolyte; *9*—anode

the electrolyte, we have the electrochemistry of melts or molten media; and when the space between the electrodes is filled with a gas, we have the electrochemistry of gases.

An electrochemical system may be in an equilibrium (Fig. I.2*a*) or nonequilibrium state (Fig. I.2*b* and *c*). A system producing electrical energy as a result of chemical transformations is called a *chemical source of electricity* or *galvanic cell* (Fig. I.2*b*). In this case the electrode from which electrons are given up to the external circuit is called the *negative electrode*, or the *negative pole* of the cell. The electrode which accepts electrons from the external circuit is called the *positive electrode*, or the *positive pole* of the cell.

An electrochemical system in which chemical reactions are induced by external electrical energy is called the *electrolyzer* or *electrolytic cell* (Fig. I.2*c*). Here the electrode which accepts electrons from the reactants is called the *anode*, and the electrode which donates electrons to the participants is called the *cathode.* That part of the electrolyte in the immediate vicinity of the anode is the *anolyte*, and analogously the *catholyte* is the electrolyte surrounding the cathode.

Since the loss of electrons implies oxidation, and the acceptance of electrons implies reduction, it may be said that the anode is the electrode at which the reaction of oxidation occurs, and the cathode is the electrode at which reduction takes place. Hence the anode is also the negative, and the cathode the positive pole of a galvanic cell.

The above considerations concerning the difference between electrochemical and chemical reactions and the subject matter and scope of electrochemistry are consistent with the views first expounded by L. V. Pisarzhevsky. The concept of "electrochemical science" may, however, be somewhat extended. Some authors regard as belonging to electrochemistry the phenomena associated with the electrochemical properties of colloids, with chemical reactions caused by the action of light or a flux of radioactive particles and giving rise to a potential difference, with electrochemical processes occurring in animal and plant organisms, etc. It seems more correct at present to distinguish between colloid electrochemistry, photoelectrochemistry, etc., applying the term electrochemistry to systems involving mutual conversion of chemical and electrical energies.

This classification is believed to be justified since each of these branches has its own distinctive features. In bioelectrochemical processes, for instance, the conversion of the energy of a biochemical reaction into electricity, as a rule, proceeds without the participation of metals, but spatial separation of the charged particles is also required.

From the diagram shown in Fig. I.2 it follows that a true electrochemical system is a circuit composed of series-connected conductors of the first and second classes. From this point of view, an electrical discharge in gases cannot be classed as a purely electrochemical process because the gases exhibit mixed electronic and ionic conduction in these conditions and many fundamental laws of electrochemistry are not applicable to them.

I.2. THERMODYNAMICS OF ELECTROCHEMICAL SYSTEMS

I.2.1. RELATION BETWEEN HEAT EFFECT, FREE ENERGY CHANGE AND ELECTRICAL ENERGY IN REVERSIBLE SYSTEMS

The quantitative relationship between chemical and electrical energies, the study of which constitutes one of the main tasks of theoretical electrochemistry, can be established from the thermodynamic treatment of electrochemical systems.

Suppose the following reversible and isothermal reaction takes place in an electrochemical system:

$$\nu_A A + \nu_B B + \ldots \underset{\longleftarrow}{\overset{\pm ze}{\rightleftharpoons}} \nu_L L + \nu_M M + \ldots \pm \bar{q} \qquad (I.2)$$

where ν_A, ν_B, ν_L,
and ν_M = stoichiometric numbers
z = number of elementary charges e ($e = 4.803 \times \times 10^{-10}$ electrostatic units) corresponding to stoichiometric reaction
$\bar{q}$ = thermochemical heat effect of reaction corresponding to q_P in an isobaric and q_V in an isochoric process.

If the electromotive force (emf) measured in conditions of a reversible reaction (I.2) is E, then the quantity of electricity taken up or produced by an electrochemical system will be equal to the product Eze or, on the gram-molecular basis, to EzF. The quantity F is known as the *Faraday number* (*Faraday's constant*) or the *faraday*. It is defined as the product of Avogadro's number $N_A = 6.02 \times 10^{23}$ by an elementary charge e ($F = N_A e$) and is equal to 96,500 coulombs (C).

Since in an electrochemical system the energy changes corresponding to a current-producing process manifest themselves not as the heat effect but in the form of electrical energy, it is natural to assume that

$$Eze = \bar{q} \tag{I.3}$$

or

$$EzF = \bar{Q} \tag{I.4}$$

where $\bar{Q} = N_A \bar{q}$. This assumption was made by Thomson, and therefore Eq. (I.4) is known as the *Thomson principle*. This principle however is not valid in a general case. A correct relation between heat effect and electrical energy can be found as follows.

For reversible systems the first and the second law of thermodynamics are usually expressed by means of four independent equations:

$$U = TS - PV \tag{I.5}$$
$$H = U + PV \tag{I.6}$$
$$\mathfrak{F} = U - TS \tag{I.7}$$
$$G = H - TS \tag{I.8}$$

where U = internal energy of system
H = enthalpy, or heat content
$\mathfrak{F}$ = Helmholtz free energy
G = Gibbs free energy
T = absolute temperature
S = entropy
P = pressure
V = volume.

The internal energy U is defined as the total differential of the entropy S and volume V:

$$dU = T\,dS - P\,dV, \quad U = f(S, V) \tag{I.9}$$

and, consequently,

$$dH = T\,dS + V dP, \qquad H = f(S, P) \tag{I.10}$$
$$d\mathfrak{F} = -S\,dT - P\,dV, \quad \mathfrak{F} = f(T, V) \tag{I.11}$$
$$dG = -S\,dT + V dP, \quad G = f(T, P) \tag{I.12}$$

All these equations take into account only the work $W_m = PV$ done against the external forces. In a general case, apart from doing (or being subjected to) mechanical work, a system may also do (or be subjected to) some other type of work W. Equations (I.9) through (I.12) must therefore be rewritten thus:

$$dU = T\,dS - P\,dV - dW \tag{I.13}$$
$$dH = T\,dS - V\,dP - dW \tag{I.14}$$
$$d\mathfrak{F} = -S\,dT - P\,dV - dW \tag{I.15}$$
$$dG = -S\,dT + V\,dP - dW \tag{I.16}$$

where the negative sign for an infinitesimal work dW signifies that if this work is done by the system, its potential energy will fall off. From Eqs. (I.13) through (I.16) we have:

$$-dU_{S,V} = dW \tag{I.17}$$
$$-dH_{S,P} = dW \tag{I.18}$$
$$-d\mathfrak{F}_{T,V} = dW \tag{I.19}$$
$$-dG_{T,P} = dW \tag{I.20}$$

that is, a change (decrease) in any of the principal thermodynamic functions for the given characteristic parameters is equal to work differing from the work done against external forces. If the work W is electrical in nature, then

$$W = zFE \tag{I.21}$$

and

$$dW = zF\ dE \tag{I.22}$$

For a reversible isothermal reaction (I.2)

$$d\mathfrak{F}_{T,V} = -zF\ dE_{T,V} \tag{I.23}$$

and

$$dG_{T,P} = -zF\ dE_{T,P} \tag{I.24}$$

or

$$\Delta\mathfrak{F}_{T,V} = -zFE_{T,V} \tag{I.25}$$
$$\Delta G_{T,P} = -zFE_{T,P} \tag{I.26}$$

Thus, the electrical energy produced (or consumed) in electrochemical processes is determined by the change of the Helmholtz free energy or Gibbs free energy rather than by the heat effect of the corresponding chemical reaction (the Thomson principle). The change of

the Helmholtz free energy or Gibbs free energy is a function of heat effects, which may be introduced into Eqs. (I.25) and (I.26), this making it possible to determine the range of applicability of the Thomson principle. According to expressions (I.11) and (I.12)

$$\left(\frac{\partial \mathfrak{F}}{\partial T}\right)_V = -S \tag{I.27}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{I.28}$$

Using Eqs. (I.7) and (I.8), we therefore get:

$$\mathfrak{F} = U + T\left(\frac{\partial \mathfrak{F}}{\partial T}\right)_V \tag{I.29}$$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \tag{I.30}$$

or

$$\Delta \mathfrak{F}_V = -\bar{Q}_V + T\left(\frac{\partial \Delta \mathfrak{F}}{\partial T}\right)_V \tag{I.31}$$

$$\Delta G_P = -\bar{Q}_P + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \tag{I.32}$$

where $\bar{Q}_V$ and $\bar{Q}_P$ are thermochemical heat effects at constant volume and at constant pressure, respectively.

Equations (I.29) through (I.32) are known as the *Gibbs-Helmholtz equations*. For electrochemical systems these equations should be rewritten in the form:

$$zFE_V = \bar{Q}_V + zFT\left(\frac{\partial E}{\partial T}\right)_V \tag{I.33}$$

and

$$zFE_P = \bar{Q}_P + zFT\left(\frac{\partial E}{\partial T}\right)_P \tag{I.34}$$

From Eqs. (I.33) and (I.34) it follows that the Thomson principle is valid only in those cases where $\partial E/\partial T = 0$ or $T = 0°K$. The emf of electrochemical systems is measured at temperatures much higher than absolute zero, and $\partial E/\partial T \neq 0$, i.e., this principle has limited application [for rough calculations, where the temperature coefficient of the cell emf is small (see Table I.1)]. The temperature coefficient of the cell emf may be either positive or negative. If $\Delta E/\Delta T > > 0$, then $zFE > \bar{Q}$, and the system will transform into electrical energy not only the heat corresponding to the heat effect of the reaction but also the additional amount of heat, equal to $zFT\,(\partial E/\partial T)$, which is taken up from the surroundings (see cells 2, 3, and 5 in Table I.1). In the case of adiabatic work of the system, i.e., under conditions of thermal insulation, when no exchange of heat with the

TABLE I.1

Thermodynamic Characteristics of Some Electrochemical Systems

Cell No.	Cell	t, °C	E, V	$\bar{Q}_P$, kcal/g-mole	$\frac{\Delta E}{\Delta T} \times 10^4$, V/deg	ΔG, kcal/g-mole
1	$Zn/ZnSO_{4(sat)}//CuSO_{4(sat)}/Cu$	15	1.0934	55.189	—4.29	—50.440
2	Hg, $Hg_2O/0.01N$KOH// $0.01N$ KCl/Hg_2Cl_2, Hg	18.5	0.1636	—3.710	8.37	—3.770
3	Ag, AgCl/HCl/Hg_2Cl_2, Hg	25.0	0.0465	—1.270	3.39	—1.050
4	$Zn/100H_2O$, $ZnCl_2$/AgCl, Ag	0.0	1.015	51.880	—4.02	—46.820
5	$Pb/Pb(CH_3COO)_2//Cu(CH_3COO)_2/Cu$	15	0.4764	16.520	4.10	21.960

surroundings is possible, the temperature of the system falls. If $\Delta E/\Delta T < 0$, then $zFE < \bar{Q}$ and part of the reaction heat will be dissipated or spent on heating the cell in an adiabatic process (see cells 1 and 4 in Table I.1). If $\Delta E/\Delta T > 0$ and $\bar{Q} < 0$, the cell will absorb all the necessary quantity of heat from the surroundings or, when the cell is thermally insulated, it will cool off (see cells 2 and 3 in Table I.1).

For quantitative calculations of the cell emf taking account of the heat equivalent of electrical energy and the Faraday number, Eqs. (I.33) and (I.34) may be rewritten as:

$$E_V = \frac{\bar{Q}_V}{23{,}063z} + T\left(\frac{\partial E}{\partial T}\right)_V \tag{I.35}$$

and

$$E_P = \frac{\bar{Q}_P}{26{,}063z} + T\left(\frac{\partial E}{\partial T}\right)_P \tag{I.36}$$

For the practical use of Eqs. (I.33) through (I.36) it is necessary to bear in mind that they are applicable only to reversible electrochemical systems. For this reason, when studying the temperature dependence of the emf one must avoid using electrochemical systems with a liquid junction, since the diffusion potential arising on this junction (*liquid junction potential*) is not an equilibrium potential (see page 150). A small inaccuracy in emf measurements arising from the presence of a liquid junction potential leads to considerable errors, since at $z = 1$ an error of 1 millivolt is equivalent to 23 cal. Similarly, an error of 1×10^{-6} V/deg in the determination of the temperature coefficient is equivalent to about 7 cal at 25°C and $z = 1$.

I.2.2. RELATION BETWEEN ELECTRICAL AND CHEMICAL ENERGIES IN REVERSIBLE CELLS

The electrical energy involved in electrochemical systems is associated with chemical transformations and hence with the chemical energy of the reaction. Like any other form of energy—mechanical, thermal, electrical, etc.—chemical energy may be represented as a product of two factors: intensivity and extensivity, or capacity. By analogy with electrical energy (where the intensivity factor is the electrical potential, and the capacity factor, the quantity of electricity), the chemical energy of each component of a system under consideration, for example, its *i*th component, is resolved into the chemical potential μ_i (intensivity factor) and the mass m_i, or the number of particles of a given species n_i (capacity factor). Instead of Eq. (I.9) we may write the expression

$$dU = TdS - PdV + \Sigma \mu_i dn_i \qquad \text{(I.37)}$$

and the summation should be carried out over all the participants of the electrochemical reaction.

Equation (I.37) may also be represented as

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N} dV + \Sigma \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n'} dn_i \qquad \text{(I.38)}$$

where $(\partial U/\partial n_i)_{S, V, n'} = \mu_i$, $N = \Sigma n_i$, and n' signifies that the masses of all the components, except the ith one, remain constant.

Equations (I.10) through (I.12) may be transformed in a similar way:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P, N} dS + \left(\frac{\partial H}{\partial P}\right)_{S, N} dP + \Sigma \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n'} dn_i \qquad \text{(I.39)}$$

$$d\mathfrak{F} = \left(\frac{\partial \mathfrak{F}}{\partial T}\right)_{V, N} dT + \left(\frac{\partial \mathfrak{F}}{\partial V}\right)_{T, N} dV + \Sigma \left(\frac{\partial \mathfrak{F}}{\partial n_i}\right)_{T, V, n'} dn_i \qquad \text{(I.40)}^{1)}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \Sigma \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n'} dn_i \qquad \text{(I.41)}$$

Here the third term on the right-hand side of each of these equations corresponds to the change of chemical energy in a corresponding chemical reversible process, i.e., to the quantity $\Sigma \mu_i dn_i$. Hence, the chemical potential is a partial quantity and may be defined as a change in the thermodynamic function with respect to the number of particles of a given component provided that the number of particles of all other components and the parameters (entropy, tempera-

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[1)] From the expression (I.40) at constant temperature and volume it follows that

$$d\mathfrak{F}_{T, V} = \Sigma \left(\frac{\partial \mathfrak{F}}{\partial n_i}\right)_{T, V, n'} dn_i = \Sigma \mu_i \, dn_i$$

and

$$\mathfrak{F}_{T, V} = \Sigma \mu_i n_i$$

ture, pressure) characterizing a particular thermodynamic function are constant. It may be considered, as a certain approximation, that the chemical potential expresses the fraction of energy (internal energy, heat content, Helmholtz free energy or Gibbs free energy) per one particle or per unit mass if instead of the number of particles n_i use is made of the mass m_i of a given component. At constant temperature and pressure Eq. (I.41) reduces to

$$dG_{T,P} = \Sigma \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} dn_i = \Sigma \mu_i \, dn_i \tag{I.42}$$

or, after integration,

$$G_{T,P} = \Sigma \mu_i n_i \tag{I.43}$$

Differentiation of Eq. (I.43) gives

$$dG_{T,P} = \Sigma \mu_i dn_i + \Sigma n_i d\mu_i \tag{I.44}$$

From Eqs. (I.42) and (I.44) it follows that

$$\Sigma n_i d\mu_i = 0 \tag{I.45}$$

Equation (I.45) is called the *Gibbs-Duhem equation.* A comparison of Eqs. (I.24) and (I.42) shows that if the reaction taking place in a system corresponds to a current-producing (electrochemical) process, then

$$-zF \, dE = \Sigma \mu_i dn_i \quad \text{or} \quad zFE = -\Sigma \mu_i n_i \tag{I.46}$$

Equation (I.46) expresses a relation between the electrical energy of an electrochemical system and the chemical energy of a chemical change occurring in the system. This equation also reflects the relation between the electrical energy and the chemical composition of an electrochemical system.

I.2.3. IRREVERSIBLE ELECTROCHEMICAL SYSTEMS

We have assumed so far that an electrochemical system is in a state of thermodynamic equilibrium. If a measurable electric current I is passed through a system, the latter is no longer thermodynamically reversible and begins to function as a galvanic or electrolytic cell. Since the useful work done by the system under irreversible conditions is always less than its maximum work in a reversible process, the electrical energy generated by the galvanic cell will be less than the maximum work:

$$(zFE_I)_{gc} < W \tag{I.47}$$

or

$$(zFE_I)_{gc} < zFE \tag{I.48}$$

The quantity $(E_I)_{gc}$ is called the *voltage of the galvanic cell* and designated as U_{gc}. The energy corresponding to the difference zF $(E - -U_{gc})$ is dissipated as heat. Conversely, if the electrochemical system operates as an electrolytic cell under a current load I, then not all the electrical energy imparted to the system but only part of it is converted into the useful energy of the chemical reaction. In this case

$$(zFE_I)_{ec} > W \tag{I.49}$$

or

$$(zFE_I)_{ec} > zFE \tag{I.50}$$

The quantity $(E_I)_{ec}$ is termed the *cell voltage* and is denoted as U_{ec}. The energy corresponding to the difference zF $(U_{ec} - E)$ is dissipated as heat.

In contrast to the reversible value of the emf, E, the E_I quantities, i.e. U_{gc} and U_{ec}, cannot be estimated on the basis of thermodynamic calculations alone.

PART ONE

Equilibrium in Electrolyte Solutions

CHAPTER 1

Theory of Electrolytic Dissociation

1.1. PRINCIPLES OF THE THEORY OF ELECTROLYTIC DISSOCIATION

The first quantitative theory of electrolyte solutions, i.e., solutions of substances capable of conducting electricity, was suggested by S. Arrhenius in the period 1883-87. The theory was further developed in the works of W. Ostwald, P. Walden, L. Pisarzhevsky and others. It is based on the following three postulates:

1. Certain substances, called *electrolytes*, are capable of splitting into oppositely charged particles (ions) when dissolved in appropriate solutions, say, in water (which was originally referred to in Arrhenius' theory).

Splitting of electrolytes into ions on dissolution was named the process of electrolytic dissociation. Hence the name for Arrhenius' theory—the *theory of electrolytic dissociation.*

This basic postulate had been put forward by many investigators before Arrhenius. Grotthus wrote as far back as 1818: "...the splitting up of molecules (for example, molecules of water and the molecules of common salt dissolved in it) into elementary particles takes place even before an electric current is applied to the solution. In the liquid itself there must operate constant galvanism owing to the presence of different types of elementary particles...". Dissolution of the salt was treated by Grotthus as "the ability of the salt to split up into its polar electrical elementary particles".

The number of ions ν formed on dissociation of an electrolyte molecule as well as the magnitude and sign of the charge z of these ions depend on the nature of the electrolyte. Electrolytes may accordingly be classified into the following types:

(a) *Binary electrolytes* dissociating into two ions. If both ions are univalent as, for example, in the dissociation of sodium chloride NaCl, then such an electrolyte is called *uni-univalent* and designated as a 1 : 1 electrolyte; if the ions are bivalent, as is the case with zinc

sulphate $ZnSO_4$, the latter is called a *bi-bivalent* electrolyte (2 : 2 electrolyte), etc. Binary electrolytes are symmetrical electrolytes.

(b) *Ternary electrolytes* giving rise to three ions on dissociation. These include uni-bivalent (e.g. Na_2SO_4) and bi-univalent (e.g. $CaCl_2$) electrolytes. They are designated, respectively, as 1 : 2 and 2 : 1 electrolytes.

(c) *Quaternary electrolytes* dissociating into four ions. To this group belong uni-trivalent (e.g. K_3PO_4) and tri-univalent [e.g. $Al(NO_3)_3$] electrolytes. They are abbreviated, respectively, to 1 : 3 and 3 : 1 electrolytes. Ternary and quaternary electrolytes are non-symmetrical.

2. Electrolytes do not dissociate completely into ions on dissolution. Only a certain part of the dissolved molecules is present as ions. The fraction of the total number of molecules which are dissociated into ions at equilibrium is the *degree of dissociation* α. The degree of dissociation is equal to the ratio of the number of molecules n dissociated into ions to the total number of dissolved molecules N (ionized n and unionized n_a molecules):

$$\alpha = \frac{n}{N} = \frac{n}{n + n_a}$$

The degree of dissociation of a substance dissolved in a given solvent depends (at constant temperature and pressure) on the nature and concentration of this substance. If a substance does not dissociate into ions on dissolution ($n = 0$, $n_a = N$, $\alpha = 0$), it cannot be regarded as an electrolyte. If α is close to unity, then $n \simeq N$ and the substance is a strong electrolyte. For many chemical compounds $0 < \alpha \ll 1$, and hence $n \ll N$. Such compounds are weak electrolytes.

The theory of electrolytic dissociation relates the qualitative changes observed in electrolyte solutions when the concentration increases or decreases to the change of the degree of dissociation. The degree of dissociation is treated by this theory as one of the principal quantitative characteristics of an electrolyte solution.

Another quantitative characteristic is the *dissociation constant* K of an electrolyte. The relation between the dissociation constant K and the degree of dissociation α can be established by using, for example, a binary electrolyte MA, which dissociates according to the reaction

$$MA = M^{z+} + A^{z-}$$

Let the total concentration of the electrolyte be c, the concentration of undissociated molecules c_a, that of cations c_+, and of anions c_-. Then

$$K = \frac{c_+ c_-}{c_a} \qquad (1.1)$$

If the degree of dissociation at the given total concentration c is α_c, then $c_+ = c_- = \alpha_c c$, and $c_a = (1 - \alpha_c)\, c$. Hence

$$K = \frac{\alpha_c^2 c}{1 - \alpha_c} \tag{1.2}$$

If the concentration c is replaced by the inverse quantity, the dilution V, then

$$K = \frac{\alpha_V^2}{1 - \alpha_V V} \tag{1.3}$$

Equations (1.2) and (1.3) were derived by Ostwald and are known as *Ostwald's dilution law.*

Unlike the degree of dissociation, the dissociation constant does not depend on concentration and is determined primarily by the nature of an electrolyte. At $\alpha_c \ll 1$ the degree of dissociation α_c and the dissociation constant K are related as follows:

$$\alpha_c = \sqrt{\frac{K}{c}} = \sqrt{KV} \tag{1.4}$$

3. No forces of interaction operate between ions, and electrolyte solutions behave like ideal gas systems. Though not stated explicitly by the authors of the theory, this principle underlies all the quantitative relationships involved.

Using these three postulates, the theory of electrolytic dissociation successfully explained a number of properties of solutions, provided their quantitative characteristics and interpreted numerous experimental facts and laws.

1.2. APPLICATIONS OF THE THEORY OF ELECTROLYTIC DISSOCIATION

The theories of electrical conductance and diffusion in electrolyte solutions, the osmotic theory of generation of emf, etc., have been developed on the basis of the concepts of electrolytic dissociation.

1.2.1. THE OSMOTIC PROPERTIES OF ELECTROLYTES

Electrolytic solutions are known to exhibit certain anomalies as regards osmotic pressure, vapour pressure above the solution, variation of boiling and freezing points (elevation of the boiling point and depression of the freezing point) with composition, etc. The effects observed in all these cases are different from those to be expected at a particular mole fraction of the solute, and correspond to higher concentrations of the latter. In this connection van't Hoff suggested introducing an empirical factor i ($i > 1$) by which the concentration should be multiplied to obtain agreement between

theory and experiment. If this factor is taken into account, the equation for osmotic pressure π in electrolyte solutions, for example, will assume the following form

$$\pi = iRTc \tag{1.5}$$

where R is the gas constant.

The physical meaning of the empirical factor i, known as the *isotonic factor*, remained obscure until the theory of electrolytic dissociation was developed. In the Arrhenius theory this factor is regarded as a measure of the increase in the total number of particles in the solution which occurs when the solute dissociates into ions. The isotonic factor must therefore be a function of the degree of dissociation. Thus, if one molecule of an electrolyte splits into ν ions and α is the degree of dissociation, then the true number of particles given by the product ic (where c is the molar concentration of the electrolyte) will be:

$$ic = (1 - \alpha_c)\, c + \nu\alpha_c c \tag{1.6}$$

whence

$$i = 1 - \alpha_c + \nu\alpha_c = 1 + \alpha_c\,(\nu - 1) \tag{1.7}$$

Equation (1.7) relates the isotonic factor (van't Hoff's factor) to the degree of dissociation. For strong binary electrolytes $\alpha_c = 1$ and $\nu = 2$, from which $i = 2$, and consequently the actual concentration of particles will be twice as high as the molar concentration of the solute.

1.2.2. THERMOCHEMICAL EFFECTS IN ELECTROLYTIC SOLUTIONS

As was found by Hess in 1842, the thermal effects of chemical reactions in electrolytic solutions also show certain anomalies. Thus, the heats of neutralization of strong acids by strong bases are constant and practically independent of the nature of an acid or base, despite the fact that their mixing produces entirely different salts. For instance, the neutralization of aqueous nitric acid by potassium hydroxide yields a solution of potassium nitrate:

$$HNO_3 + KOH = KNO_3 + H_2O + \bar{Q}_1 \tag{1.8}$$

and the neutralization of aqueous hydrochloric acid by sodium hydroxide results in a solution of sodium chloride:

$$HCl + NaOH = NaCl + H_2O + \bar{Q}_2 \tag{1.9}$$

In spite of this, the measured heats of formation of both salts are practically the same, i.e., $\bar{Q}_1 = \bar{Q}_2$.

The mixing of salt solutions involves no noticeable thermal effect, though exchange reactions may give rise to new compounds, as, for example, in a reaction between potassium chloride and sodium sulphate:

$$2KCl + Na_2SO_4 = K_2SO_4 + 2NaCl + \overline{Q}$$

The heat effects for this and many other similar reactions are practically nil.

According to the theory of electrolytic dissociation such experimental thermochemical regularities are accounted for by the fact that salts as well as strong acids and bases almost completely dissociate into ions in water and in a number of other solvents, i.e., for these substances $\alpha_c = 1$. Under these conditions the reaction of neutralization reduces to the formation of water from H^+ and OH^- ions; the base cation and the acid anion remain unchanged and are present as free ions as before. Indeed, if we rewrite the above reactions of neutralization in an ionic form

$$H^+ + NO_3^- + K^+ + OH^- = K^+ + NO_3^- + H_2O \quad (1.10)$$
$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O \quad (1.11)$$

and cancel out those particles that undergo no change, the process that is actually taking place in both cases will then be the reaction between hydrogen and hydroxyl ions:

$$H^+ + OH^- = H_2O \quad (1.12$$

involving a characteristic thermal effect. When solutions of different salts with degrees of dissociation close to unity are mixed, the resulting solution will retain the free ions from the initial solutions. No chemical transformation takes place in this case and hence no heat effect is observed.

1.2.3. CHEMICAL EQUILIBRIUM IN ELECTROLYTIC SOLUTIONS

The theory of electrolytic dissociation has made it possible to supply scientific definitions for the concepts "acid", "base", "solution buffer capacity", to develop the theory of indicators, to elucidate the processes of step dissociation, hydrolysis of salts, etc.

Some examples of the application of this theory to chemical equilibrium in solutions are discussed below.

Electrolytic Dissociation of Water. The dissociation of water proceeds according to the scheme:

$$H_2O = H^+ + OH^- \quad (1.13)$$

and its dissociation constant may be expressed as

$$K = \frac{c_{H^+} c_{OH^-}}{c_{H_2O}} \tag{1.14}$$

Since the degree of dissociation of water is very small, c_{H_2O} may be taken as constant and included in the dissociation constant:

$$K c_{H_2O} = c_{H^+} c_{OH^-} = K_w \tag{1.15}$$

Equation (1.15) is called the *ionic product of water*. At 25°C, $K_w = 10^{-14}$ and consequently

$$c_{H^+} c_{OH^-} = 10^{-14}$$

According to the theory of electrolytic dissociation hydrogen ions are carriers of acidic properties and hydroxyl ions are carriers of basic properties. A solution is neutral, that is, neither acidic nor alkaline, if $c_{H^+} = c_{OH^-} = \sqrt{K_w}$. At 25°C, the quantity K_w is equal to 10^{-14} so that for a neutral solution $c_{H^+} = 10^{-7}$ gram-ions/litre and $c_{OH^-} = 10^{-7}$ gram-ions/litre. If use is made of the term pH suggested by Sorensen in 1909, which is a negative common logarithm of the hydrogen ion concentration ($pH = -\log c_{H^+}$), a pH value of 7 will then correspond to neutrality. A solution is acidic at $pH < 7$ and alkaline at $pH > 7$.

It must be remembered that a solution of pH = 7 will be neutral only at 25°C. In using the pH scale one should keep in mind that the dissociation constant [1] of water K_w varies greatly with temperature, increasing almost hundredfold between 20 and 100°C:

t, °C	20	30	60	70	80	90	100
$K_w \times 10^{14}$	0.681	1.47	9.61	15.8	25.1	38.0	55.0

For this reason the point pH 7 will correspond to an acid solution at temperatures below 25°C, and to an alkaline solution at temperatures above 25°C.

Since the hydrogen ion concentration serves as a measure of acidity, the strongest in a series of acids will be the one whose hydrogen ion concentration is the highest at equal molar concentration. The hydrogen ion concentration is defined as $\alpha_c c$ and hence α_c is a measure of strength of an acid. It is quite obvious that α_c is also a measure of strength of a base.

In addition to the dissociation constant K and the ionic product K_w of water, there is still another important characteristic of water, namely the *equilibrium constant* K_{H_2O} corresponding to the reaction

$$H_2O + H_2O \underset{k}{\overset{\vec{k}}{\rightleftharpoons}} H_3O^+ + OH^-$$

[1] The indicated values of K_w correspond to the ionic product of water expressed in terms of ionic activity instead of ionic concentration (see Chap. 2).

The value of this constant

$$K_{H_2O} = \frac{\vec{k}}{\overleftarrow{k}}$$

often called the *autohydrolysis constant*, at 25°C, is 2×10^{-6} mole·litre^{-1}; $\vec{k}$ and $\overleftarrow{k}$ are the rate constants for a forward and a reverse reaction, respectively.

Buffer Capacity of Solutions. The hydrogen ion concentration (pH) plays an important part in many phenomena and processes. Certain physicochemical and biochemical phenomena occur only at definite pH values. Numerous chemical reactions proceed in the desired direction only at some definite pH value, which must therefore be kept constant.

The resistance of a solution to pH change on addition of an acid or alkali is known as *buffer action* (solutions exhibiting this behaviour are called *buffer solutions*). The effectiveness of buffering of a solution is measured by its *buffer capacity* β, which may be defined as the amount b of an alkali (or an acid) in gram-equivalents required to cause a unit change of pH. The buffer capacity β may be expressed in differential form as follows:

$$\beta = \frac{db}{d\text{pH}} \tag{1.16}$$

For pure water the number of gram-equivalents, b, of alkali added must be equal to the concentration of alkali cation c_{M+}. Since the concentrations of hydrogen and hydroxyl ions are equal for pure water ($c_{H+} = c_{OH-}$) and a strong alkali is completely dissociated, then

$$c_{M+} = b = c_{OH^-} - c_{H+} = \frac{K_w}{c_{H+}} - c_{H+}$$

Differentiation with respect to pH (i. e., with respect to $-\log c_{H+}$) gives [1]

$$\beta = \frac{db}{d\text{pH}} = 2.303\left(c_{H+} + \frac{K_w}{c_{H+}}\right) = 2.303\,(c_{H+} + c_{OH-}) \tag{1.17}$$

This equation is valid for any aqueous solution of a strong acid and a strong base (alkali). Indeed, if a certain amount b (g-eq) of a strong base MOH is added to a solution of a strong acid HA, then this amount b will correspond to the concentration of metal ions, $b = c_{M+}$, as the degrees of dissociation of the acid and base and of the resulting salt are equal to unity. According to the law of electroneutrality

$$c_{M+} + c_{H+} = b + c_{H+} = c_{A-} + c_{OH-}$$

[1] Differentiation is easily carried out if one takes into account that

$$2.303\text{pH} = -\ln c_{H+} \quad \text{and} \quad d\ln c_{H+} = \frac{dc_{H+}}{c_{H+}}$$

or

$$b = c_{A^-} + c_{OH^-} - c_{H^+}$$

from which, taking into account that the concentration of acid anions c_{A^-} is independent of the amount of base added, we obtain for the buffer capacity

$$\beta = \frac{db}{d\text{pH}} = 2.303\,(c_{H^+} + c_{OH^-})$$

which is identical to Eq. (1.17). From Eq. (1.17) it follows that the buffer capacity of pure water (or a solution containing a salt of a strong base or acid) is very low. Buffer capacity becomes noticeable if an excess of a strong acid or base is present in the solution.

Buffer capacity increases in the case of solutions of weak acids or weak bases, especially in the presence of the corresponding salts. If we add b g-eq of a strong base to a solution containing originally a g-eq of a weak acid (a being greater than b), then

$$a = c_{HA} + c_{A^-} \tag{1.18}$$

and

$$b = c_{A^-} + c_{OH^-} - c_{H^+} \tag{1.19}$$

On the basis of Eq. (1.18) the dissociation constant of the acid, which is equal to

$$K_{HA} = \frac{c_{H^+} c_{A^-}}{c_{HA}} \tag{1.20}$$

may be represented as

$$K_{HA} = \frac{c_{H^+} c_{A^-}}{a - c_{A^-}} \tag{1.21}$$

Solving the last equation for c_{A^-} and substituting its value into Eq. (1.19), we get for the number of gram-equivalents of the base:

$$b = \frac{aK_{HA}}{K_{HA} + c_{H^+}} + c_{OH^-} - c_{H^+}$$

whence it is easy to arrive at the buffer capacity

$$\beta = \frac{db}{d\text{pH}} = 2.303 \left[\frac{aK_{HA} c_{H^+}}{(K_{HA} + c_{H^+})^2} + c_{H^+} + c_{OH^-} \right] \tag{1.22}$$

Since $\frac{aK_{HA} c_{H^+}}{(K_{HA} + c_{H^+})^2} > 0$, the buffer capacity of a solution of a weak acid and its salt is always higher than that of water, a salt solution, or a solution of a strong acid or a strong base, for which formula (1.17) is valid. In this case the quantity β must depend on the dissociation constant K_{HA} of the weak acid. Solutions containing mixtures of weak

acids and their salts (or weak bases and their salts) are used to prepare so-called *standard buffer solutions*. Analysis of Eq. (1.22) shows that the solution of the weak acid in question must have the greatest buffer capacity in the pH range close to pK_{HA}, i.e., $\beta = \beta_{max}$ at $pH = pK_{HA}$. For example, for acetic acid (HAc) $K_{HAc} = 1.76 \times 10^{-5}$, $pK_{HAc} = 4.77$ and the maximum buffer capacity will be observed at pH values around 4.8. A standard buffer solution of high buffer capacity in a wide pH range can be prepared by selecting acids with different values of pK_{HA}. Buffer solutions are used for measuring the pH of solutions as well as for carrying out various chemical processes at constant pH values.

1.3. SHORTCOMINGS OF THE THEORY OF ELECTROLYTIC DISSOCIATION

In its early stages the theory of electrolytic dissociation made great advances within a short period of time. It should however be noted that, along with the brilliant successes achieved, there have been weighty failures pointing to certain drawbacks of the theory.

The degree of dissociation α_c, which determines the fraction of ionized molecules in a solution, should be the same under the given conditions (irrespective of the method of its measurement). According to its physical meaning α_c must always be between 0 and 1.

TABLE 1.1

The Degree of Dissociation of Some Electrolytes Based on Measurements of Conductance (α_1) and Osmotic Pressure (α_2)

Electrolyte	c, g-eq/litre	α_1	α_2
KCl	5×10^{-3}	0.956	0.963
KCl	1×10^{-2}	0.941	0.943
KCl	2×10^{-2}	0.922	0.918
KCl	5×10^{-2}	0.889	0.885
$BaCl_2$	1×10^{-1}	0.751	0.788
$MgSO_4$	1×10^{-1}	0.434	0.324
$La(NO_3)_3$	1×10^{-6}	0.920	0.946
$La(NO_3)_3$	1×10^{-5}	0.788	0.865
$La(NO_3)_3$	1×10^{-4}	0.635	0.715

How well this agrees with experiment can be seen from Table 1.1, which compares the values of α_c found by measurements of osmotic pressure and electrical conductance for a number of electrolytes.

The best agreement between the degrees of dissociation α_c determined by the indicated methods is found in the case of dilute solutions of uni-univalent electrolytes. Increasing the electrolyte concentration or passing to ions of higher valency affects the agreement between the values of α_1 and α_2 (see Table 1.1), the difference exceeding possible experimental errors.

The values of α_c for solutions of hydrochloric acid calculated on the basis of measurements of conductance (α_1) and electromotive force (α_3) are listed in Table 1.2.

TABLE 1.2

The Degree of Electrolytic Dissociation of HCl from Conductance (α_1) and Electromotive Force (α_3) Measurements

c_{HCl}, mole/litre	α_1	α_3
0.003	0.986	0.990
0.08	0.957	0.880
0.3	0.903	0.773
3.0	—	1.402
6.0	—	3.4
16.0	—	13.2

The discrepancy between the values of α_c obtained by these methods also increases with increasing electrolyte concentration, α_3 being greater than unity in the range of high concentrations. From the viewpoint of the Arrhenius theory, this result would make no sense because in this case a greater number of molecules must have been dissociated into ions than are actually present in the solution. For instance, in 6.0*N* HCl the number of particles split into ions is found to exceed by a factor of 3.4 the number of all the HCl molecules present and in 16*N* HCl, by a factor of 13 and something. Hence, here the degree of dissociation α_c loses the physical meaning ascribed to it by the Arrhenius theory.

A second quantitative characteristic of an electrolyte in the Arrhenius theory is the dissociation constant, which must remain constant for a given electrolyte at a specified temperature and pressure, irrespective of the concentration of the solution. The values of the dissociation constant for several solutions of differing concentration are given in Table 1.3. Only for very weak electrolytes (e.g., solutions of ammonia and acetic acid) does the dissociation constant remain more or less constant upon dilution. For strong electrolytes (e.g., potassium chloride and magnesium sulphate) it varies by tens of times and cannot therefore be regarded as a constant.

TABLE 1.3

The Dissociation Constants of Some Electrolytes at Various Concentrations

c, g-eq/litre	KCl $K\times10^2$	$MgSO_4$ $K\times10^3$	NH_4OH $K\times10^5$	CH_3COOH $K\times10^5$
1.000×10^{-4}	1.28	2.35	1.06	—
2.000×10^{-4}	1.96	3.23	—	—
2.879×10^{-4}	—	—	—	1.885
1.000×10^{-3}	4.56	6.01	1.56	—
1.151×10^{-3}	—	—	—	1.850
2.303×10^{-3}	—	—	—	1.849
5.000×10^{-3}	10.51	10.46	—	—
1.000×10^{-2}	15.10	13.29	1.68	—
1.842×10^{-2}	—	—	—	1.849
3.685×10^{-2}	—	—	—	1.851
5.000×10^{-2}	35.97	24.66	—	—
1.000×10^{-1}	53.49	33.34	1.92	—

The theory of electrolytic dissociation thus appears to be applicable only to dilute solutions of weak electrolytes. The behaviour of concentrated solutions of weak electrolytes and of solutions of strong electrolytes of any concentration cannot be described quantitatively on the basis of the theory proposed by Arrhenius. The degree of dissociation does not have the physical meaning assigned to it by the Arrhenius theory. The dissociation constant is not constant, but is a function of the solution concentration.

A fundamental deficiency of the Arrhenius theory is the fact that it does not indicate the factors responsible for the ionization of electrolytes in solution. The process of ionization however requires a considerable amount of energy. This can be exemplified by such a typical electrolyte as potassium chloride. It is known that the bonding between the atoms in a KCl molecule is electrostatic and that potassium and chloride ions are located at the points of its crystal lattice. The bond energy for ions in a single molecule may be represented as an integral

$$\int_r^\infty \frac{e^2}{r^2}\,dr = \frac{e^2}{r} \tag{1.23}$$

where r = distance between ionic centres in molecule
e = ionic charge.

Assuming r equal to 2.79 Å, which corresponds to the KCl lattice constant, we get

$$\frac{e^2}{r} = \frac{(4.803\times10^{-10})^2}{2.79\times10^{-8}}$$

or, in terms of a gram-molecule,

$$N_A \frac{e^2}{r} = 4.98 \times 10^{12} \text{ erg/mole} = 119.0 \text{ kcal/mole}^{1)}$$

At the same time the average amount of thermal energy stored in molecules at 25°C is about 3.4 kcal/mole. Using these values and applying Boltzmann's formula, one can express the number of particles n, possessing an amount of energy sufficient to split them into ions, through the total number of particles N of potassium chloride

$$n = Ne^{-\frac{119}{3.4}} = Ne^{-35} = N \cdot 10^{-15}$$

The degree of dissociation, defined as the ratio n/N, is then equal to 10^{-15}.

The value of α for an aqueous solution of potassium chloride is known to be close to unity, i.e., almost each of its molecules is dissociated into free ions. The process of dissolution must evolve an amount of energy sufficient to break the bonds existing in the molecule before its dissociation into ions. However, neither the source nor the nature of this additional energy is considered by the classical theory of electrolytic dissociation.

The limited range of applicability of the theory of electrolytic dissociation, the disagreement between experimental values of α and K and their physical meaning within the framework of this theory, and the obscure explanation of the main process could not but cause criticism. The essence of this criticism and the possible ways of improvement of the theory of solutions were outlined by Mendeleyev. He wrote in "Fundamentals of Chemistry" that the critical flaw in the theory of electrolytic dissociation as well as the cause of all its shortcomings lies in the neglect of the interaction between solute particles and between solute and solvent. He pointed out that not only the processes of dissociation but also those of formation of new compounds involving the participation of solvent molecules are essential to solutions. These ideas were further developed at the close of the last and the first quarter of the present century by a number of workers (Konovalov, Kablukov, Kistyakovsky, Pisarzhevsky, Noyes and others). They formed the basis of the modern theory of solutions. The quantitative formulation of the idea of ion-ion and ion-solvent interactions was given much later.

[1)] The lattice energy of crystalline KCl will of course differ from this value. Precise calculations will not however change the final results to any considerable extent.

CHAPTER 2

Theory of Ionic Interaction

2.1. IONIC ACTIVITY AND ACTIVITY COEFFICIENT

An analogy may be found in the development of the theory of electrolytic solutions and the theory of the gas state of aggregation. In either case it was originally thought that the system behaved like an ideal one and that no forces of interaction existed between its constituent particles. The application of the laws obtained on the basis of these conceptions led to considerable disagreement between theory and experiment. In connection with this, it was suggested that the simple equation of the gas state

$$PV = RT$$

be replaced by other, more complicated, equations taking into account the forces of interaction between the particles. One of these was the van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are corrections, respectively, for the forces of mutual attraction and the final volume of gas particles or, to a first approximation, for repulsive forces.

The development of the theory of solutions could have followed a similar path. But it took quite a different turn. The form of the equations describing the properties of solutions remained unaltered, but their applicability to real systems was ensured by introducing quantities taken from experiment in place of the conventional quantities characterizing a system (pressure, concentration). Thus, vapour pressure is replaced by a quantity known as *volatility* or *fugacity*, and concentration by a quantity called *activity*. For example, according to Lewis, Eq. (1.20), which defines the dissociation constant of a weak acid and is valid for ideal systems, can be made applicable to real systems by rewriting it as follows:

$$K_{\mathrm{HA}(a)} = \frac{a_{\mathrm{H}^+} a_{\mathrm{A}^-}}{a_{\mathrm{HA}}} \tag{2.1}$$

It can easily be seen that though this equation coincides in form with Eq. (1.20), it correctly describes the behaviour of a real solution. This is because Eq. (2.1), as distinct from Eq. (1.20), contains

not the concentrations of ions c_+ and c_- and of undissociated electrolyte molecules c_a, but the corresponding activities a_+, a_- and a_a. Activity values are selected so that the dissociation constant remains the same, irrespective of the total concentration of the electrolyte. Unlike the dissociation constant K, given by Eq. (1.20), the dissociation constant K_a will therefore be a true constant for a given electrolyte at a definite temperature.

There are three ways of expressing activities, corresponding to the three methods for expressing the quantitative composition of a solution (Table 2.1).

TABLE 2.1

Methods Used for Expressing the Composition of a Solution Through Concentration and Activity

Scale	Definition	Symbol for	
		concentration	activity
Molarity	$\frac{\text{mole}}{\text{litre of solution}}$	c	a_c
Molality	$\frac{\text{mole}}{\text{kg of solvent}}$	m	a_m
Mole fraction (rational scale)	$\frac{\text{number of moles of solute}}{\text{total number of moles in solution}}$	N	a_N

The concept of activity differs from that of concentration in that it includes the forces of interaction existing in solutions and independent of the nature and concentration of the solute particles. Activity may therefore be defined as the product of concentration and a certain variable known as the *activity coefficient*:

$$a_c = cf_c, \; a_m = mf_m, \; a_N = Nf_N \tag{2.2}$$

where f_c = molar activity coefficient
f_m = molal activity coefficient
f_N = rational activity coefficient.

The activity coefficient contains a correction for the forces of interaction.

The activity of a single ionic species, and hence its activity coefficient, cannot be determined from experimental data. Equations that could be employed to find activities contain the product of the activities of all the ions of a given electrolyte rather than the activity of any one ionic species. For this reason the concept of *mean activity* had to be introduced, which is defined as the geometrical

mean of the activities of the ions constituting a given electrolyte. For an electrolyte dissociating into ν_+ positive and ν_- negative ions, the mean activity is given by

$$a_\pm = (a_+^{\nu_+} a_-^{\nu_-})^{\frac{1}{\nu_+ + \nu_-}} \tag{2.3}$$

and for a binary electrolyte

$$a_\pm = \sqrt{a_+ a_-} \tag{2.4}$$

The mean activity coefficients of an electrolyte dissociating into ν_+ and ν_- ions can be determined in a similar way:

$$f_\pm = (f_+^{\nu_+} f_-^{\nu_-})^{\frac{1}{\nu_+ + \nu_-}} \tag{2.5}$$

and, accordingly, of a binary electrolyte

$$f_\pm = \sqrt{f_+ f_-} \tag{2.6}$$

The same concepts may also be applied to concentrations. For example, if the composition of a solution is to be expressed through molality, the following relations can be written, which hold for any type of electrolyte:

$${}_m a_\pm = m_\pm {}_m f_\pm = [(\nu_+ m_+)^{\nu_+} (\nu_- m_-)^{\nu_-}]^{\frac{1}{\nu_+ + \nu_-}} ({}_m f_+^{\nu_+} {}_m f_-^{\nu_-})^{\frac{1}{\nu_+ + \nu_-}} \tag{2.7}$$

or for a binary electrolyte

$${}_m a_\pm = \sqrt{m_+ {}_m f_+ m_- {}_m f_-} \tag{2.8}$$

In the case of infinite dilution the forces of interaction between the particles of a solute become vanishingly small. The ionic activity here coincides with concentration, and the activity coefficient is equal to unity, no matter in which way it is expressed, i.e.,

$$\begin{gathered} (a_c \to c)_{c \to 0} \\ (a_m \to m)_{m \to 0} \\ (a_N \to N)_{N \to 0} \end{gathered} \tag{2.9}$$

and

$$(f_c = f_m = f_N \to 1)_{c,\, m,\, N \to 0}$$

At infinite dilution (also at low concentrations of the electrolyte, with a certain degree of approximation) the difference in the activity coefficients f_c, f_m and f_N is small and it may be assumed in many calculations that

$$f_c = f_m = f_N = f$$

The state of an infinitely dilute solution could therefore be taken as a standard one irrespective of the way in which concentration and activity are expressed. This choice however cannot be considered appropriate because of the resulting uncertainty in the values of concentrations of solutes. Instead, as the standard state we choose the state of an imaginary solution in which the concentration, activity, and activity coefficient expressed by the same method are each equal to unity. On the molarity basis, this corresponds to a solution one litre of which contains one gram-molecule of the solute ($c = 1$), a_c and f_c being also equal to unity. If the molality system is used, a solution in which one gram-molecule of the solute is dissolved in one kilogram of the solvent will correspond to the standard state; in this case not only m is unity, but also $a_m = 1$ and $f_m = 1$. And, finally, if the solution composition is expressed in terms of mole fractions, the standard state will be a pure solute for which $N = 1$, $a_N = 1$, and $f_N = 1$.

If we assume, under these conditions, that for a given electrolyte the standard values of ionic activities satisfy the relation

$$a_{+st}^{\nu_+} a_{-st}^{\nu_-} = 1 \tag{2.10}$$

then the following expression can be obtained for the total activity of the electrolyte a_{el}

$$a_{el} = a_+^{\nu_+} a_-^{\nu_-} = a_\pm^{\nu_+ + \nu_-} \tag{2.11}$$

Equation (2.11) is valid for a completely or partially dissociated electrolyte. If $\alpha \neq 1$, the total activity of the electrolyte a_{el} will coincide in magnitude with the activity of its undissociated molecules a_a.

When use is made of activity coefficients, Eq. (2.1) can be rewritten for the dissociation constant of a weak acid in the following form:

$$K_{\mathrm{HA}(a)} = \frac{c_{\mathrm{H}^+} f_{\mathrm{H}^+} c_{\mathrm{A}^-} f_{\mathrm{A}^-}}{c_{\mathrm{HA}} f_{\mathrm{HA}}} = \frac{c_{\mathrm{H}^+} c_{\mathrm{A}^-}}{c_{\mathrm{HA}}} \cdot \frac{f_{\mathrm{H}^+} f_{\mathrm{A}^-}}{f_{\mathrm{HA}}} \tag{2.12}$$

From Eq. (1.20) it follows that

$$\frac{c_{\mathrm{H}^+} c_{\mathrm{A}^-}}{c_{\mathrm{HA}}} = K_{\mathrm{HA}}$$

and, consequently,

$$K_{\mathrm{HA}(a)} = K_{\mathrm{HA}} \frac{f_{\mathrm{H}^+} f_{\mathrm{A}^-}}{f_{\mathrm{HA}}} \tag{2.13}$$

or

$$\mathrm{pK}_{\mathrm{HA}(a)} = \mathrm{pK}_{\mathrm{HA}} - 2 \log f_{\pm(\mathrm{HA})} + \log f_{(\mathrm{HA})} \tag{2.14}$$

Since the activity coefficient of uncharged particles varies with solution composition much slower than that of ions, and is but slightly different from unity in the range of moderate concentrations,

Eq. (2.14) can be replaced by an approximate expression:

$$pK_{HA(a)} = pK_{HA} - 2 \log f_{\pm(HA)} \qquad (2.15)$$

Equations (2.12) to (2.15) establish a relation between the values of the dissociation constant expressed in terms of activity and concentration. A similar relationship can also be established for other cases of chemical equilibrium in ideal and real solutions. For example, the pH value for real solutions must be equal to the negative common logarithm of the activity of hydrogen ions:

$$pH_{(a)} = - \log a_{H+} \qquad (2.16)$$

Substituting the product $c_{H+}f_{H+}$ for a_{H+}, we get

$$pH_{(a)} = pH - \log f_{H+} \qquad (2.17)$$

Equation (2.17) however is applicable only to dilute solutions, for which the activity coefficients of individual ions can be determined.

2.2. EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS. IONIC STRENGTH OF SOLUTIONS

Activity coefficients can be found by comparing analytical concentrations with those quantities which should be substituted into equations for electrolytic solutions in order to provide agreement with experiment. It must be remembered that activity coefficients may be different, depending on the state of the electrolyte and hence on the nature of the forces of interaction. The character of interaction (and the relevant correction factor) depends on whether the electrolyte solution is at equilibrium or under the action of an external electric field, or in the state of unestablished equilibrium when its composition is not completely homogeneous. Activity coefficients characterize interaction forces in equilibrium conditions and should therefore be calculated using the results of measurements made for solutions in equilibrium, for instance, data on osmotic pressure, boiling and freezing points, electromotive force, etc.

Unlike the degree of dissociation, the activity coefficients obtained by different methods agree with each other (see Table 2.2). Correction factors reflecting the effect of interaction in nonequilibrium conditions (e.g., in the case of electronic conduction or diffusion) will be different for the same solutions. The activity coefficients given in Table 2.2 have been calculated from the results of vapour pressure measurements ($_1f_\pm$ and $_1f'_\pm$), and from freezing point depression ($_2f_\pm$) and emf ($_3f_\pm$).

The activity coefficient of all electrolytes in infinitely dilute solutions is equal to unity. It gradually decreases with increasing con-

TABLE 2.2

Mean Activity Coefficients for KCl Solutions Obtained by Different Methods at 25°C

Activity coefficient	c_{KCl}, mole/litre							
	0.001	0.01	0.05	0.1	0.5	1.0	2.0	4.0
${}_1f_\pm$	0.965	0.900	0.813	0.763	0.638	0.596	0.563	0.564
${}_1f'_\pm$	—	—	—	0.772	—	—	—	—
${}_2f_\pm$	0.965	0.899	0.809	0.762	—	—	—	—
${}_3f_\pm$	0.965	0.899	0.815	0.764	0.644	0.597	0.569	0.581

centration and becomes a minimum at a certain concentration depending on the nature of the electrolyte and the solution temperature. Further rise of concentration leads to an increase of the activity coefficient, which may even exceed unity for highly concentrated solutions; this is exemplified by $MnCl_2$ solutions:

c_{MnCl_2}, g-eq/litre	$f_\pm$
0.1	0.516
0.2	0.468
0.4	0.442
0.8	0.445
1.0	0.479
2.0	0.668
3.0	0.934
5.0	1.550

These results do not contradict the physical meaning of the activity coefficient as a quantity associated with forces of ionic interaction. Indeed, at infinite dilution, when the ions are too far apart, no forces of interaction exist between them. Since the solution behaves like an ideal system and the concentration does not differ from the activity, the activity coefficient must be equal to unity. As the concentration increases the ions approach one another and forces of interaction arise between them, mainly the forces of mutual attraction, and the activity coefficient decreases. At definite concentrations there also arise repulsive forces in addition to the forces of attraction. When these forces balance, which is equivalent, to a certain extent, to the absence of ionic interaction, the activity coefficient will again be equal to unity. At still higher concentrations the repulsive forces become predominant and the activity coefficient acquires values greater than unity.

A study of the dependence of activity coefficients, and also of activities, on the solution composition led Lewis and his coworkers to the discovery of a number of important empirical laws and rules.

For one thing, they found that at low concentrations the mean activity coefficients of an electrolyte are determined by the valency of the ions formed and are independent of other properties. For instance, under these conditions the mean activity coefficients of potassium bromide, sodium nitrate and hydrochloric acid are equal. It was also found that the mean activity coefficients for very dilute solutions depend on the total concentration of all the electrolytes present and their valencies, but not on their chemical nature. This observation led to the concept of *ionic strength* suggested by Lewis and Randall. The ionic strength of solutions J is defined as the half sum of the products of the concentration of ions by the square of their valency

$$J = \frac{1}{2} \Sigma c_i z_i^2 \tag{2.18}$$

From Eq. (2.18) it follows that the ionic strength of uni-univalent electrolytes coincides in magnitude with their concentration, while for other electrolytes it is always higher than the concentration. For example, in the case of a strong 2 : 2-valent electrolyte with molarity c (assuming that $\alpha = 1$ and $c_+ = c_- = c$) the ionic strength is equal to the quadruple concentration

$$J = \frac{1}{2} (c \cdot 2^2 + c \cdot 2^2) = 4c$$

It has also been established that for dilute solutions of strong electrolytes the logarithm of the mean activity coefficient of the electrolyte depends linearly on the square root of its ionic strength

$$\log f_\pm = -h\sqrt{J} \tag{2.19}$$

This law breaks down at increased concentrations. Experimental data for a wide range of concentrations are presented in Figs. 2.1 and 2.2 (see page 52).

2.3. THERMODYNAMIC FOUNDATIONS OF THE THEORY OF IONIC INTERACTION

Activity coefficients were originally introduced as empirical quantities which can be found by studying the effects characteristic of solutions in equilibrium. For this purpose use is made of such phenomena as the variation of vapour pressure above solution with a change in electrolyte concentration, the dependence of reversible emf on the solution composition, and others. Since the necessity of introducing activity coefficients into equations for ideal systems is due to the difference between real and ideal solutions, their value is independent of the method of determination and is the same for any type of equilibrium with given conditions and composition. For this reason the same activity coefficients may be used to describe different equilibrium phenomena. Tables containing empirical activity coefficients

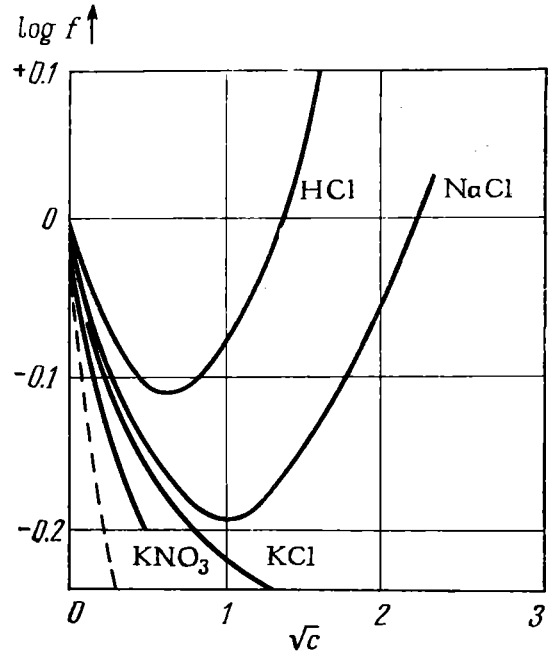


Fig. 2.1. Concentration dependence of the mean activity coefficient of a 1 : 1-valent electrolyte. [The dashed line has been plotted on the basis of Eq. (2.59)]

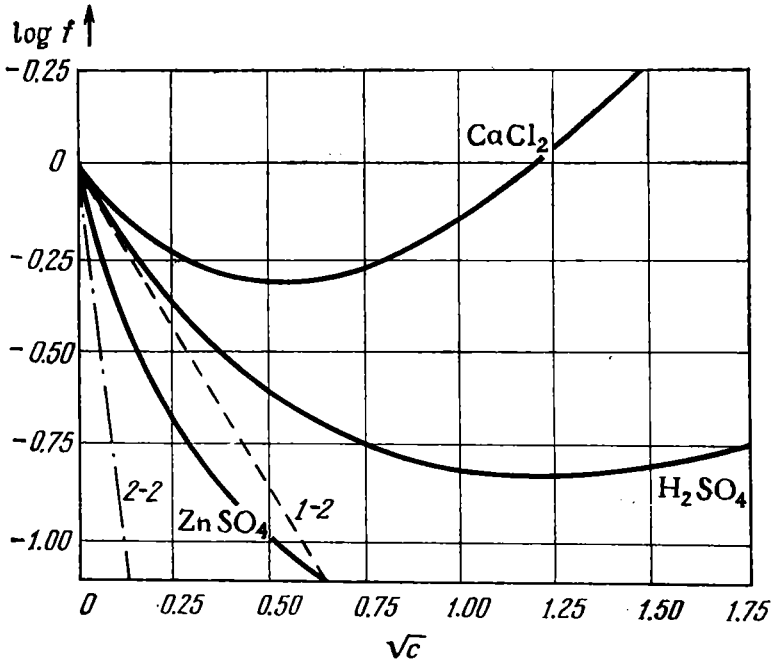


Fig. 2.2. Concentration dependence of the mean activity coefficient of 1 : 2- and 2 : 2-valent electrolytes. [The dashed lines have been plotted on the basis of Eq. (2.58)]

are of great value. At the same time, within the framework of the Lewis theory activity coefficients are only formal correction factors which bear no direct relation to the nature of solutions and do not lend themselves to theoretical calculations. Real solutions are known to differ from ideal ones by the presence of additional energy of interaction between their constituent particles. Activity coefficients as a quantitative expression of the change of electrolyte properties when switching from ideal solutions to real ones must be functions of the energy of interaction between the particles.

Activity coefficients can be related to the energy of interaction by means of general thermodynamic equations. The free energy G of a real solution must be greater than that of an ideal solution, $\bar{G}$, by an amount corresponding to the energy of ionic interaction, G^*:

$$G = \bar{G} + G^* \tag{2.20}$$

From Eq. (2.20) it follows that

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,\,T,\,n'} = \left(\frac{\partial \bar{G}}{\partial n_i}\right)_{P,\,T,\,n'} + \left(\frac{\partial G^*}{\partial n_i}\right)_{P,\,T,\,n'} \tag{2.21}$$

If we denote the quantity $\partial G^*/\partial n_i$ by g_i^* and take into account Eq. (I.42), then Eq. (2.21) may be replaced by

$$\mu_i = \bar{\mu}_i + g_i^* \tag{2.22}$$

where μ_i and $\bar{\mu}_i$ = chemical potentials of an ith component in a real and an ideal solution, respectively

g_i^* = partial energy of interaction referred to the ith ion.

Since, by Eqs. (I.16) and (I.41),

$$\left(\frac{\partial G}{\partial P}\right)_{T,\,N} = V \tag{2.23}$$

it follows that

$$\left(\frac{\partial \mu_i}{\partial p_i}\right)_{T,\,N} = v_i \tag{2.24}$$

where p_i = partial pressure

v_i = partial molecular volume of an ith component.

According to the law of ideal gases

$$v_i = \frac{kT}{p_i}$$

and, consequently [1],

$$\bar{\mu}_i = \mu_i^0 + kT \ln p_i \tag{2.25}$$

---

[1] The composition of a solution is expressed here by the number of particles (molecules, atoms or ions) per unit volume. The equation therefore contains Boltzmann's constant k in place of the gas constant R, which is N_A times as great as the former.

where μ_i^0 is the integration constant or the so-called *standard chemical potential.* Equation (2.25) can be transformed to read:

$$\bar{\mu}_i = \mu_{i(c)}^0 + kT \ln c_i \tag{2.26}$$

if we consider that

$$p_i = kTc_i$$

and introduce the notation

$$\mu_{i(c)}^0 = \mu_i^0 + kT \ln kT$$

Equation (2.26) rewritten for a real system will have the form

$$\mu_i = \mu_i^0 + kT \ln a_i \tag{2.27}$$

or (since $a_i = c_i f_i$)

$$\mu_i = \mu_i^0 + kT \ln c_i + kT \ln f_i \tag{2.28}$$

Comparing Eqs. (2.26) and (2.28), we find that

$$\mu_i = \bar{\mu}_i + kT \ln f_i \tag{2.29}$$

Comparison of expressions (2.22) and (2.29) shows that

$$kT \ln f_i = g_i^* = \left(\frac{\partial G^*}{\partial n_i}\right)_{P,\,T,\,n'} \tag{2.30}$$

and that the activity coefficient can be determined from the interaction energy g_i^*. The latter can be calculated if the mutual arrangement of ions in solution and the forces operating between them are known. Neither of these is known with sufficient accuracy, and therefore one has to make certain assumptions in order to solve the problem.

2.3.1. DISTRIBUTION OF IONS IN SOLUTION ACCORDING TO ARRHENIUS AND GHOSH

The third postulate of the Arrhenius theory defines electrolyte solutions as ideal systems. According to this postulate it should be assumed that the ions in solution are arranged in a random fashion and the interionic forces are equal to zero. This assumption leads (irrespective of the composition of a solution) to a single value of activity coefficient, namely to the quantity $f_\pm$ equal to unity. This conclusion contradicts experiment and indicates the invalidity of the solution model proposed by Arrhenius.

A different view on the nature of electrolyte solutions was expressed by Ghosh, an Indian scientist, in the period between 1918 and 1920. According to Ghosh's theory the ions in solution are arranged in the same strict order as in the crystal lattice of the corresponding solid body. The difference lies mainly in that the distance between two neighbouring ions is found to be greater in solution than in the

original crystal. In this case the process of solution is identified with swelling. The spaces between the ions are filled with solvent molecules and the interionic forces are weakened as a result of increase of the dielectric constant and of the distance between the ions. Ionic interactions are electrostatic in origin.

On the basis of these and some other postulates Ghosh succeeded in deriving formulas for calculating the free energy of solution, activity coefficient, heats of dilution, etc. Within the range of moderate concentrations these formulas are in qualitative agreement with experiment. The premises of Ghosh's theory however do not agree with present-day data on the structure of solutions and many of its inferences are in conflict with experimental facts. For example, from this theory it follows that the temperature dependence of the potential energy of a solution is contingent on the variation in the dielectric constant of the solution. In fact the potential energy of a solution depends directly on temperature. The results of X-ray and other methods of studying the structure of solutions do not support Ghosh's ideas that the crystal lattice of the original substances is preserved in electrolytic solutions. The discrepancies between the Ghosh theory and experiment should primarily be attributed to the fact that no account is taken in this theory of the role of thermal motion which is bound to distort the ordered lattice-like structure of the ions.

2.3.2. THE DEBYE-HÜCKEL THEORY

The Debye-Hückel Model of Electrolytic Solutions. The modern theory of electrolytic solutions, the basic propositions of which were formulated by Debye and Hückel in 1923, arose as an attempt to improve Ghosh's theory. Debye and Hückel attempted to build up such a concept of solutions that would reflect ion-ion interactions and the effect of thermal motion. It should be noted that Ghosh was not the only predecessor of Debye and Hückel. Van Laar, Sutherland Bjerrum, Hertz, Milner and others had anticipated in their works some of the basic propositions of the Debye-Hückel theory. But these earlier works attracted little attention at the time and none of them influenced noticeably the development of the theory of solutions.

Debye and Hückel accept Ghosh's basic idea that the distribution of ions peculiar to crystals, where each ion is surrounded predominantly by ions of opposite sign, is retained in solution. As distinct from crystals, however, due to thermal motion the ions in solution do not retain their fixed position in the lattice points, but are arranged spherically around an arbitrarily selected central ion. Considering that the principal type of motion in solutions is translational (not vibrational, as in crystals), the sphere surrounding the central ion cannot always contain the same ions. There is continuous interchange between the ions contained in the sphere and other ions. Such a sta-

tistical sphere around the central ion is called the *ionic atmosphere* or *ionic cloud.* All the ions in solution are equal in all respects; each of them is surrounded by an ionic atmosphere and at the same time each central ion makes part of the ionic atmosphere of some other ion (Fig. 2.3). It is the existence of ionic atmospheres that, according to Debye and Hückel, distinguishes real electrolytic solutions from ideal ones. The extra energy G^* of real solutions must therefore

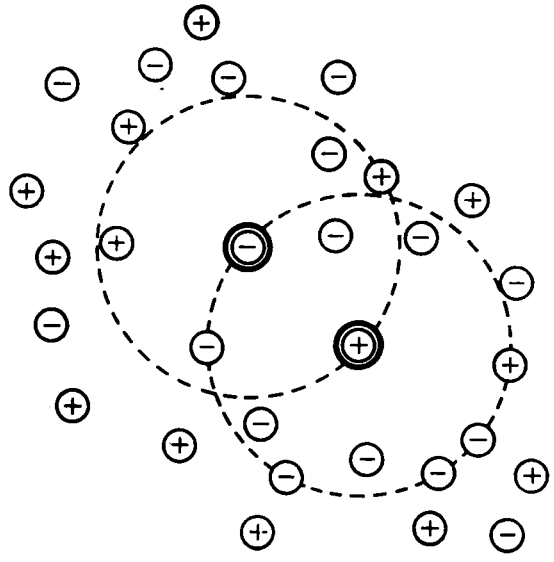


Fig. 2.3. The Debye-Hückel model of the ionic atmosphere

reflect the cumulative effect of ionic atmospheres on central ions. Calculation of activity coefficients reduces to finding an expression for this energy in terms of properties of solutions accessible to direct measurement.

Calculation of the Energy of Ionic Interaction and Activity Coefficients. The energy associated with the ionic atmosphere is electrical in origin. It must therefore be a function of the charge density and the potential produced by the ionic atmosphere. Since the latter is a statistical formation, we may ignore the discrete distribution of charges and use the Poisson equation to relate the mean charge density ρ to the corresponding mean value of the potential ψ

$$\nabla^2\psi = -\frac{4\pi}{D}\rho \tag{2.31}$$

where D = dielectric constant

∇^2 = Laplacian operator, which may be expressed in rectangular coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2.32}$$

Poisson's equation contains two unknown quantities, ρ and ψ. To find them, it is necessary to have a second equation connecting these two variables. Debye and Hückel derived the required equation as follows.

Let the volume of a solution be V and let there be, per unit volume, N_1 ions of type 1, each bearing charge ez_1, N_2 ions of type 2 with charge ez_2, N_i of type i with charge ez_i, and N_k of the last type k

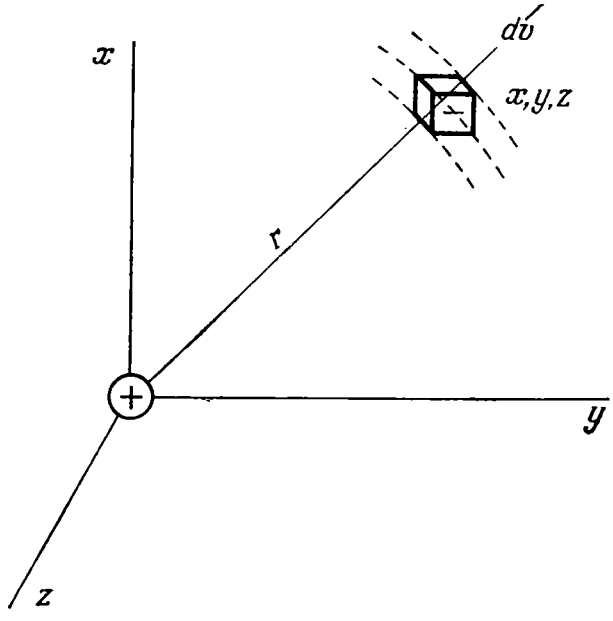


Fig. 2.4. Distribution of charges around a central ion

with charge ez_k. Since the number of charges of the positive ions of an electrolyte is equal to that of the negative ions,

$$\Sigma N_i ez_i = 0 \text{ and } \Sigma N_i z_i = 0 \tag{2.33}$$

The law of electroneutrality is valid not only for a solution as a whole, but also for any given element of its volume sufficiently large as compared to the ionic size. If the selected volume of the solution is equal to unity, then

$$\Sigma n_i ez_i = 0 \text{ and } \Sigma n_i z_i = 0 \tag{2.34}$$

where n_i is the number of ions of the species i per unit volume (say, one millilitre). However, the charge of a certain volume element dV situated in the vicinity of an ion and moving together with it through the solution during the thermal motion (Fig. 2.4) will be different from zero due to the presence of an ionic atmosphere. If the *central ion* (or *reference ion*) located at the coordinate origin is positively charged, the volume element dV will then have an excess negative charge. Assuming that the Boltzmann principle is applicable to

the ionic distribution in solution and that the forces operating between the ions are electrostatic in nature, one can express the number of negative ions in the volume element dV as follows:

$$dn_- = n_- e^{\frac{ez_i}{kT}\psi} dV$$

and the number of positive ions as

$$dn_+ = n_+ e^{-\frac{ez_i}{kT}\psi} dV$$

The charge of the volume element will then be

$$\left(ez_- n_- e^{\frac{ez_-}{kT}\psi} - ez_+ n_+ e^{-\frac{ez_+}{kT}\psi}\right) dV$$

and the charge density

$$ez_- n_- e^{\frac{ez_-}{kT}\psi} - ez_+ n_+ e^{-\frac{ez_+}{kT}\psi}$$

Taking into account that there are different ionic species in the solution and ascribing to the valency of an ion a sign corresponding to its charge, one may write

$$\rho = \Sigma ez_i n_i e^{-\frac{ez_i}{kT}\psi} \tag{2.35}$$

Substitution of the value of ρ from Eq. (2.35) into the Poisson equation yields

$$\nabla^2\psi = -\frac{4\pi}{D} e\Sigma z_i n_i e^{-\frac{ez_i}{kT}\psi} \tag{2.36}$$

Equation (2.36) in its general form is difficult to solve. To simplify it, Debye and Hückel made an assumption that $ez_i\psi \ll kT$, i.e., that the electrostatic interaction is small compared to the thermal energy. Expanding the exponential function into a series

$$e^{-\frac{ez_i}{kT}\psi} = 1 - \frac{ez_i}{kT}\psi + \frac{1}{2!}\left(\frac{ez_i}{kT}\psi\right)^2 \ldots \tag{2.37}$$

they confined their consideration to the first two terms and obtained the following equation for ρ

$$\rho = \Sigma ez_i n_i - \frac{e^2}{kT}\Sigma z_i^2 n_i \psi \tag{2.38}$$

The first term on the right-hand side of Eq. (2.38) is equal to zero according to the law of electrical neutrality, from which

$$\rho = -\frac{e^2}{kT}\Sigma z_i^2 n_i \psi$$

and, consequently,

$$\nabla^2\psi = \frac{4\pi e^2}{DkT}\Sigma z_i^2 n_i \psi \tag{2.39}$$

Introducing a new variable χ defined by

$$\chi = \sqrt{\frac{4\pi e^2}{DkT} \Sigma z_i^2 n_i} \tag{2.40}$$

one has

$$\nabla^2 \psi = \chi^2 \psi \tag{2.41}$$

The quantity χ, or, more precisely $1/\chi$, is of great value in the theory of electrolytic solutions, as will be shown below. Taking into account the spherical symmetry of an ionic atmosphere, we may write, instead of $\nabla^2\psi$,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \tag{2.42}$$

Substituting this value of $\nabla^2\psi$ into Eq. (2.42) gives

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \chi^2 \psi \tag{2.43}$$

where r is the distance from the central ion to the point where the electrostatic potential ψ is determined.

The general solution of this differential equation is

$$\psi = A_1 \frac{e^{-\chi r}}{r} + A_2 \frac{e^{\chi r}}{r} \tag{2.44}$$

The integration constants A_1 and A_2 are evaluated from the boundary conditions. As follows from the basic laws of electrostatics, the potential ψ vanishes at sufficiently great distances from the central ion ($\psi \to 0$ as $r \to \infty$), this being the first boundary condition. This condition would be satisfied only if $A_2 = 0$; otherwise, with increasing distance from the central ion the electrostatic potential would shoot up to infinity, i.e., $\psi \to \infty$ as $r \to \infty$ ($e^{\chi r}$ is a quantity of higher order than r). Hence, taking into account that $A_2 = 0$, Eq. (2.44) may be replaced by

$$\psi = A_1 \frac{e^{-\chi r}}{r} \tag{2.45}$$

To evaluate the integration constant A_1, it is assumed in the first approximation of the Debye-Hückel theory that ions may be regarded as material points possessing a certain charge. In this case at $r \to 0$ the potential ψ must tend to the potential ψ_i of the ion itself, i.e.,

$$\psi_{r \to 0} = \psi_i = \frac{ez_i}{Dr} \tag{2.46}$$

which is the second boundary condition.

If $e^{-\chi r}$ is expanded into a series, then

$$\psi = A_1 \frac{e^{-\chi r}}{r} = A_1 \frac{1}{r} \left(1 - \chi r + \frac{1}{2!} (\chi r)^2 - \ldots \right)$$

If $r \to 0$, all the terms of the series may be neglected as compared with unity. Then

$$\psi_{r\to 0} \to \psi_i = A_1 \frac{1}{r}$$

and one has

$$A_1 = \frac{ez_i}{D} \tag{2.47}$$

Hence, combining Eqs. (2.45) and (2.47), we get

$$\psi = \frac{ez_i}{Dr} e^{-\chi r} \tag{2.48}$$

The quantity ψ in Eq. (2.48) is the mean value of the potential at point r produced by the ionic atmosphere and the central ion. Real solutions are characterized by the potential of the ionic atmosphere ψ_{ia} which is found, using the law of the superposition of potentials, as the difference between ψ and ψ_i

$$\psi_{ia} = \psi - \psi_i = \frac{ez_i}{Dr} (e^{-\chi r} - 1)$$

To calculate the interaction energy, it is necessary to determine the potential of the ionic atmosphere at the site of the central ion, i.e., to find the limiting value of ψ_{ia} for $r \to 0$. Using the same procedure as above, i.e., expanding the exponential function into a series and neglecting the higher terms of the series, one finds that

$$\psi_{ia_{r\to 0}} \to \psi' = -\frac{ez_i}{D} \chi \tag{2.49}$$

According to Eq. (2.49), the quantity ψ' may be defined as the potential produced at the site of the central ion by an oppositely charged ion situated at a distance of $1/\chi$ from the central ion. The quantity $1/\chi$ has the dimensions of length and is referred to as the *Debye-Hückel reciprocal length* [1]. Since the potential is produced not by a single ion but by the ionic cloud as a whole, the quantity $1/\chi$ may also be called the *thickness*, or *radius*, of the ionic atmosphere. The quantity χ, and hence the radius $1/\chi$, can be computed from Eq. (2.40).

As noted above, in the first approximation of the Debye-Hückel theory (the point-charge approximation) it is assumed that the energy of ionic interaction is electrostatic in origin. It may therefore be defined as the energy of charging a central ion in the electric field of an ionic cloud. It is known that the energy of charging up a particle

[1] In fact, this quantity should be called the *Gouy length* since it was first introduced by Gouy in the theory of diffuse double layer (see below).

from a state of zero charge to a charge of q in the field ψ is equal to

$$\int_0^q \psi\, dq = \frac{1}{C}\int_0^q q\, dq = \frac{1}{2}\frac{q^2}{C} = \frac{1}{2}q\psi \qquad (2.50)$$

since $q = C\psi$, where C is capacitance.

Substituting into (2.50) the magnitude of the charge on the central ion instead of q, and the quantity ψ' from Eq. (2.49) in place of ψ yields the following expression for the energy of charging, which is equal to the energy of interaction between the central ion and the ionic atmosphere:

$$g_i^* = -\frac{ez_i}{2}\left(\frac{ez_i}{D}\chi\right) = -\frac{e^2z_i^2}{2D}\chi \qquad (2.51)$$

Using expression (2.51) in conjunction with (2.30), we get for the activity coefficient:

$$\ln f_i = -\frac{e^2z_i^2}{2DkT}\chi \qquad (2.52)$$

Substituting the value of χ from Eq. (2.40) into (2.52), one has

$$\ln f_i = -\frac{e^3z_i^2}{(DkT)^{3/2}}(\pi\Sigma n_i z_i^2)^{1/2} \qquad (2.53)$$

To express the composition of a solution in terms of the concentration in moles per litre instead of the number of particles per unit volume, the quantity n_i must be replaced by $c_iN_A/1000$. The following formula is then obtained for the activity coefficient of the ionic species i [1]:

$$\ln f_i = -\frac{e^3z_i^2}{(DkT)^{3/2}}\left(\frac{\pi N_A\Sigma c_i z_i^2}{1000}\right)^{1/2} \qquad (2.54)$$

In most cases it is necessary to know, apart from the activity coefficient f_i of a particular ionic species, the mean activity coefficient $f_\pm$ of the electrolyte, the more so that experimental data enable one to determine this quantity rather than f_i. An expression for the mean activity coefficient $f_\pm$ can be found from (2.54), taking into account that

$$\ln f_\pm = \frac{1}{\nu}\Sigma\nu_i \ln f_i$$

where ν is the number of ions into which an electrolyte molecule is dissociated; it is equal to $\Sigma\nu_i$. This expression is written down as

$$\ln f_\pm = -\frac{1}{\nu}\Sigma\nu_i e^3 z_i^2\left(\frac{\pi N_A}{1000\,(DkT)^3}\right)^{1/2}(\Sigma c_i z_i^2)^{1/2} \qquad (2.55)$$

[1] Here and further in the text the difference between the three methods of expressing the activity coefficient is ignored, which is quite permissible for dilute solutions.

Equation (2.55) can be modified, passing over from natural to decimal logarithms, by introducing the ionic strength $J = \frac{1}{2}\sum c_i z_i^2$ and lumping together all the concentration-independent quantities into a new constant h

$$\log f_{\pm} = -h\sqrt{J} \tag{2.56}$$

where

$$h = 1.283 \times 10^6 \frac{1}{\nu} \Sigma \nu_i z_i^2 (DT)^{-3/2} \tag{2.57}$$

For a binary electrolyte dissociating into ions of valencies z_- and z_+, from Eqs. (2.56) and (2.57) it follows that

$$\log f_{\pm} = -1.283 \times 10^6 \mid z_+ z_- \mid (DT)^{-3/2}\sqrt{J} \tag{2.58}$$

and for a binary 1 : 1-valent electrolyte

$$\log f_{\pm} = -1.283 \times 10^6 (DT)^{-3/2}\sqrt{J} \tag{2.59}$$

For the mean activity coefficient of a uni-univalent electrolyte at room temperature (25°C) and with a solution having a dielectric constant equal to that of water ($D = 78.3$) the following formula, corresponding to the point-charge approximation of the Debye-Hückel theory, is valid:

$$\log f_{\pm} = -0.51\sqrt{c} \tag{2.60}$$

Comparison of the Debye-Hückel Theory with Experiment. The Debye-Hückel theory permits one to obtain the same equation for the activity coefficient as has been experimentally found for dilute electrolytic solutions. The theory thus appears to be in qualitative agreement with experiment. Before proceeding to a quantitative comparison of the Debye-Hückel theory with experiment it is appropriate to consider the following assumptions underlying this theory:

1. The number of ions in solution can be determined from the analytical concentration of the electrolyte since it is considered to be completely dissociated ($\alpha = 1$). For this reason the Debye-Hückel theory is sometimes referred to as the "theory of complete dissociation". However, it may also be employed in cases where $\alpha \neq 1$. Indeed, having determined the degree of dissociation of a solution of a weak electrolyte from the intensity of light absorption, one can find the true concentration of its ions and then, by Eq. (2.60), the mean activity coefficient.

2. The distribution of ions around a central ion obeys the classical Maxwell-Boltzmann statistics. From the physical point of view it is unclear to what extent the classical statistics is applicable to an assembly of charged particles (such as ions). The Debye-Hückel theory in fact uses an ionic distribution of a type different

from the Boltzmann distribution since after the exponential function is expanded as a series the latter is terminated after the first (for unsymmetrical electrolytes) or the second term (for symmetrical electrolytes). This distribution function may thus be written as

$$n_i (z_i e\psi) = n_i \left(1 - \frac{ez_i}{kT} \psi\right) \tag{2.61}$$

A number of attempts have been made to replace this partition function by a different one, but they did not receive general recognition because they complicated the mathematical formulation without substantially improving the accuracy of calculations. The use of Eq. (2.61) in place of the Boltzmann formula is tantamount to assuming that $(z_i e\psi/kT) < 1$. The lower the concentration and valency of ions, the more valid is this inequality.

3. The ionic size may be neglected compared with interionic distances and the total volume of the solution. Ions are thus regarded as point charges and all their properties are reduced to the magnitude of charge. This assumption is valid only for dilute solutions. With increasing concentration the error becomes larger and may considerably distort the results of calculations.

4. The interaction between ions is completely determined by coulombic forces. The superposition of electrostatic forces upon thermal forces leads to such a distribution of ions in a solution which is characterized by a random spherical ionic atmosphere. This assumption is also valid only for dilute solutions. With increasing concentration the mean interionic distance decreases and, in addition to electrostatic forces, there appear other forces operating at a shorter distance, mainly van der Waals forces. The concept of ionic atmosphere must also be modified in this case since it becomes necessary to take into account not only the interactions between a particular ion and its surroundings but also between two neighbouring ions. It can be seen from Table 2.3 that as the ionic concentration and the

TABLE 2.3

Thickness of the Ionic Atmosphere for Various Types of Electrolytes as a Function of Their Concentration (Water used as solvent, $t = 25°C$)

Type of electrolyte	Thickness of ionic atmosphere, Å, at a concentration of		
	0.001 mole/litre	0.01 mole/litre	0.1 mole/litre
1 : 1	96.4	30.5	9.64
1 : 2 and 2 : 1	55.8	19.3	5.58
2 : 2	48.2	15.3	4.82
1 : 3 and 3 : 1	39.4	13.6	3.94

charge on the ions increase, the size of the ionic atmosphere becomes comparable with the ionic size, which contradicts the concept of the ionic atmosphere.

5. In creating the theory of the molecular (microscopic) structure of solutions one may use the dielectric constant, which is a macroscopic property of a system. It was assumed in calculations that the dielectric constant of a solution is equal to that of a pure solvent. These assumptions may hold true in the case of dilute solutions. For more concentrated solutions it is necessary to take into account that the dielectric constant varies with electrolyte concentration and the use of an averaged dielectric constant will not be sufficiently rigorous.

Thus, with the assumptions made by Debye and Hückel their theory can be applied only to dilute electrolytic solutions containing low-valency ions. Equations (2.52) to (2.56) and (2.58) to (2.60) correspond to this limiting case and express the so-called *Debye-Hückel limiting law* or the first approximation of the Debye-Hückel theory. For this reason, when testing the Debye-Hückel theory as the limiting law it is necessary to take into consideration that the higher the concentration of an electrolyte and the magnitude of the charges of its ions and the lower the dielectric constant of the solution, the poorer will be the agreement between this limiting law and experiment.

The Debye-Hückel limiting law yields correct values of activity coefficients for a 1 : 1-valent electrolyte (sodium chloride), particularly in very dilute solutions (Table 2.4). The fit between theory and

TABLE 2.4

Comparison of Experimental and Calculated Activity Coefficients for Solutions of NaCl and $ZnSO_4$ (Water used as solvent, $t = 25°C$)

Concentration, mole/litre	NaCl		$ZnSO_4$	
	$f_{\pm}$(exp)	$f_{\pm}$(theory)	$f_{\pm}$(exp)	$f_{\pm}$(theory)
0.0003	0.975	0.971	—	—
0.0005	—	—	0.780	0.863
0.001	0.965	0.954	0.700	0.812
0.002	0.952	0.946	0.608	0.745
0.1	0.906	0.840	0.387	0.517

experiment becomes poorer as the concentration increases. In the case of a 2 : 2-valent electrolyte (zinc sulphate) there is a discrepancy between the calculated and experimentally observed activity coefficients even at very low concentrations (see Figs. 2.1 and 2.2). For example, at a concentration of 0.01 mole per litre the divergency exceeds 30 per cent.

The experimental and calculated values of the slope of $\log f_{\pm}$ versus $\sqrt{J}$ straight lines for dilute electrolyte solutions in water-ethanol mixtures are listed in Table 2.5.

TABLE 2.5

Experimental and Calculated Values of the Slope of $\log f_{\pm}$ versus $\sqrt{J}$ Straight Lines for Various Types of Electrolytes (A mixture of water and ethyl alcohol used as solvent, $t = 25°C$)

Dielectric constant of solvent	1 : 1		1 : 2		3 : 1	
	exp.	cal.	exp.	cal.	exp.	cal.
78.8	0.50	0.50	1.40	1.08	1.52	1.51
54.0	0.89	0.89	1.74	1.76	4.00	2.65
41.0	1.31	1.32	2.74	2.65	6.10	3.98
33.8	1.90	1.80	—	—	—	—

In this case too the discrepancy between theory and experiment becomes larger with the growth of forces of interaction between the ions, i.e., as the valency of the ions increases and the dielectric constant of the solvent decreases. These and other experimental data indicate that the Debye-Hückel theory provides a correct description of the behaviour of electrolytes in the region where the assumptions involved remain valid.

Further Development of the Debye-Hückel Theory. The first attempt to improve the Debye-Hückel theory and extend the range of its application was made by the authors of the theory. In the so-called second approximation Debye and Hückel abandoned the concept of ions as point charges (assumption 3) and tried to consider ions as entities of finite size, every electrolyte being given a certain mean diameter a (with the result that assumption 4 is also changed). Assigning definite dimensions to ions, Debye and Hückel thereby took into account the repulsive forces of noncoulombic origin that prevent oppositely charged ions from approaching one another closer than a certain distance depending on the nature of the electrolyte.

In the finite-ion-size model (the second approximation), after the same transformations as in the derivation of the limiting law [1], the activity coefficient of the ionic species i is given by

$$\ln f_i = -\frac{e^2 z_i^2}{2DkT} \cdot \frac{\chi}{1+a\chi} \tag{2.62}$$

or

$$\log f_i = -\frac{h\sqrt{J}}{1+ab\sqrt{J}} \tag{2.63}$$

[1] It is assumed in calculations that the ion-size parameter a corresponds to the minimum potential energy.

where $b = \chi/\sqrt{J}$ and h retains its previous meaning. For the mean activity coefficient of an electrolyte dissociating into ν ions, of which ν_+ have a valency of z_+ and ν_- a valency of z_-, the finite-ion-size approximation leads to the equation

$$\ln f_{\pm} = -\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} \cdot \frac{e^2}{2DkT} \cdot \frac{\chi}{1 + a\chi} \tag{2.64}$$

All the equations involved in the second approximation differ from the corresponding equations of the point-charge approximation by a factor of

$$\frac{1}{1 + a\chi}$$

According to its physical meaning the parameter a depends not only on the nature of the electrolyte, the mean activity coefficient of which is to be calculated, but also on the nature of other electrolytes present in the solution since all the ions in solution participate in the formation of an ionic atmosphere. In this connection the crystallographic radii of individual substances cannot be used to determine the mean ionic diameter a of an electrolyte; it is found by experiment. Hence, in contrast to the point-charge model, the equations of the finite-ion-size model contain an empirical constant.

The best agreement with experiment was obtained by La Mer and his coworkers, who also started from the assumptions made by Debye and Hückel in their second approximation but provided a more precise mathematical solution of the basic differential equation. They showed that if one takes into account not two but more terms in a series into which the exponential function $e^{-(ez_i/kT)\psi}$ is expanded, then the equation for the mean activity coefficient of a binary electrolyte assumes the form

$$\ln f_{\pm} = -\frac{|z_+ z_-| e^2}{2DkT} \cdot \frac{\chi}{1 + a\chi} + \Sigma R_n \tag{2.65}$$

Equation (2.65) differs from Eqs. (2.62) and (2.64) in that it contains the term ΣR_n, which is the sum of the terms from the third to the fifth or sixth. If the extra terms in the series are taken into account, it will be tantamount to partial removal of the assumption that $ez_i\psi \ll kT$. Here the energy of ionic interaction becomes comparable in magnitude with the energy of thermal motion of ions, though it remains lower as before; this circumstance must extend the range of application of the theory. As shown by experimental data (see Table 2.6), Eq. (2.65) allows one and the same positive value of the mean effective diameter a to be used for calculating $f_{\pm}$, while in the finite-ion-size version of the Debye-Hückel theory the diameter a is not a constant and may be negative, which contradicts its physical meaning.

TABLE 2.6

Values of the Parameter a in Eqs. (2.62) and (2.65) at which the Calculated Value of the Mean Activity Coefficient of $ZnSO_4$ Coincides with the Experimental Value, $t = 25°C$

c	$f_\pm$	a (2.62)	a (2.65)
0.0005	0.780	—11.01	3.64
0.001	0.700	—8.22	3.68
0.002	0.608	—5.33	3.65
0.005	0.477	—2.33	3.64
0.01	0.387	—0.31	3.62

The drawback of the La Mer formula is the cumbersome procedure for calculating the sum ΣR_n. In order to facilitate calculations, special tables have been compiled, which contain values of R for various values of n, a and χ. Since the sum of the first two terms in a decreasing series is always greater than the sum of the subsequent three or four terms, it follows that

$$\frac{|z_+z_-|e^2}{2DkT} \cdot \frac{\chi}{1+a\chi} > \Sigma R_n$$

and values of the mean activity coefficient $f_\pm$ greater than unity cannot be obtained from formula (2.65), which renders it inapplicable in the case of concentrated solutions.

Semi-empirical Formulas for Calculating Activity Coefficients. A number of investigators have made an assumption that when two oppositely charged ions approach each other, ion pairs may be formed. As distinct from molecules, ion pairs are held together by coulombic forces. The probability of formation of ion pairs and also of more complex ionic assemblies is not taken into account by the Debye-Hückel theory. This is one of the reasons behind its disagreement with experiment. The degree of association of ions into pairs has been calculated and compared with experimental data. The results of this comparison show that ion association does play an important part, especially in solvents with a low dielectric constant.

Hückel tried to take into account the variation of dielectric constant with concentration of solution. Assuming ions to have a finite size but neglecting all the terms of a series into which the exponential function is expanded, except for the first-order term, Hückel inferred that the dielectric constant decreases with increasing concentration of the solution. The fall in the dielectric constant is due to the orientation of solvent dipoles around the ions with the resulting decrease in their response to the effect of the external field.

In spite of the physical plausibility of this hypothesis, the derivation of the equation for the activity coefficient given by Hückel cannot be considered correct. This follows, for example, from the fact that the decrease of the dielectric constant and the associated growth of the forces of ionic interaction progressively invalidate the assumption that $ez_i\psi \ll kT$. The equation derived by Hückel is cumbersome, but it can be replaced by a simpler one:

$$\log f_{\pm} = -\frac{h\,|z_+z_-|\sqrt{J}}{1+A\sqrt{J}} + BJ \qquad (2.66)$$

where A and B are empirical constants. If the values of A and B are chosen correctly, the Hückel formula (2.66) agrees well with experiment and is convenient for empirical calculations. It enables one to obtain positive values of $\log f_{\pm}$ in the region of strong interionic forces, where the product BJ will be greater than the first term. This makes it possible to use the Hückel formula at high concentrations.

With successively decreasing interionic forces the Hückel formula is transformed first into the formula of the Debye-Hückel finite-ion-size model (but not into the La Mer formula) and then into the Debye-Hückel limiting law. For practical calculations it is convenient to use, along with the Hückel formula, the following semi-empirical equations:

$$\log f_{\pm} = -\frac{h\,|z_+z_-|\sqrt{J}}{1+\sqrt{J}} \qquad (2.67)$$

and

$$\log f_{\pm} = -\frac{h\,|z_+z_-|\sqrt{J}}{1+\sqrt{J}} + BJ \qquad (2.68)$$

Thus, in the course of the development of the theory of solutions on the basis of the concepts introduced by Debye and Hückel it became necessary to resort to various semi-empirical equations in all cases where the electrolyte concentration was high. The derivation of theoretical equations applicable over a wide range of concentrations requires the development of more realistic conceptions of the molecular structure of electrolytes and of the nature of forces operating, along with coulombic and thermal forces, between all the particles in solution.

CHAPTER 3

Solvation and Hydration of Ions

3.1. EMPIRICAL HEATS OF HYDRATION OF ELECTROLYTES

The thermal effect observed on dissolution of one gram-molecule of a substance is called the *heat of solution* $\bar{Q}_L$. Heats of solution are usually small and may be either positive or negative. Considering that the ions in solution move independently of each other and behave as independent particles, it may be supposed that during the process of dissolution the bonds between the ions in molecules or in a crystal lattice are broken. The energy of bond rupture in the molecule and the lattice energy are high. Small heats of solution therefore indicate that the energy required to break up a crystal lattice, U_g, is generated in the process of dissolution.

Though this energy is experimentally inaccessible, it can be evaluated with sufficient accuracy by indirect methods. According to the views widely accepted at present and based on the works of Kablukov, the energy bringing about the rupture of bonds in the molecules of an electrolyte is produced by interactions between its ions and solvent particles (when water is the solvent, the process is known as *hydration*). This energy is equal to the change of the Gibbs free energy taking place during the reactions

$$M^{z+} + xH_2O = M(H_2O)_x^{z+}$$

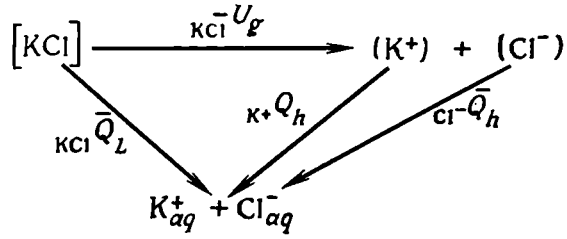
and

$$A^{z-} + yH_2O = A(H_2O)_y^{z-}$$

which give rise to hydrated ions. Similar processes are also found to occur in nonaqueous solutions, but leading to the formation of solvated ions (the process known as *solvation*). The energy effects of these two types of reactions are known as the *hydration energy* U_h and the *solvation energy* U_S, and the corresponding thermal effects as the *heat of hydration* $\bar{Q}_h$ and the *heat of solvation* Q_S (as suggested by Fajans).

The heats of hydration were first calculated by Haber and Born with the aid of cycles based on the well-known thermodynamic law (Hess's law). The application of the Born-Haber cycle is exemplified by the determination of the heat of hydration of potassium chloride.

In the first step of the cycle one gram-molecule of crystalline potassium chloride is broken up, giving rise to free gaseous potassium and chloride ions: the energy used up is the lattice energy $_{KCl}U_g$. The ions are transferred into the solvent where they form a solution of potassium chloride. This process leads to the evolution of the total heat of hydration of a potassium ion $_{K^+}\overline{Q}_h$ and a chloride ion $_{Cl^-}\overline{Q}_h$. In the second step one gram-molecule of crystalline potassium chloride is transferred directly into the same volume of solvent to form a solution of potassium chloride; this process is accompanied by the thermal effect $_{KCl}\overline{Q}_L$. The entire cycle may be represented schematically as follows:



Assuming all the steps of the cycle to be reversible and isothermal and applying Hess's law, we obtain

$$_{K^+}\overline{Q}_h + _{Cl^-}\overline{Q}_h = _{KCl}\overline{Q}_L + _{KCl}U_g \qquad (3.1)$$

Equation (3.1) allows the heat of hydration to be found [1] if the heats of solution and the lattice energy are known.

Unlike the heat of solution, the lattice energy cannot be determined experimentally. Its value is calculated by using the Born equation:

$$U_g = N_A \frac{K_M z^2 e^2}{r}\left(\frac{n-1}{n}\right) \qquad (3.2)$$

where K_M = Madelung constant depending on the mutual arrangement of positive and negative ions in the lattice (its values for various types of crystal lattice are known)

r = equilibrium distance between oppositely charged ions in a given type of lattice

n = repulsion coefficient ranging from 5 to 12 (n can be found experimentally from the compressibility of the crystal).

Kapustinsky proposed formulas which, though less precise than the Born equation, are more universal and do not require complicated calculations associated with the determination of K_M and n:

$$U_g = 256.1\nu \frac{z_+ z_-}{r_+ + r_-} \qquad (3.3)$$

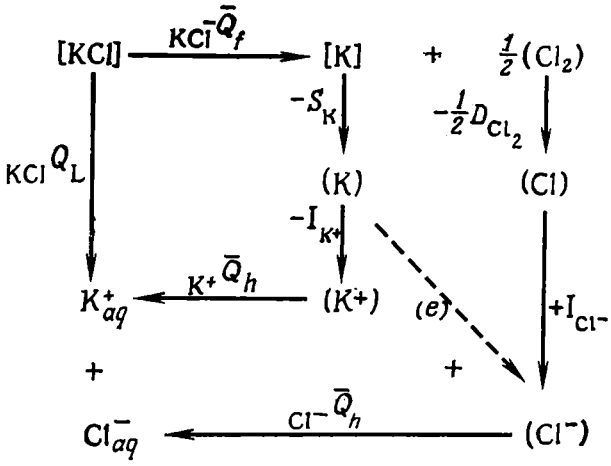
[1] In using Eq. (3.1) it should be borne in mind that it is not quite rigorous since, along with the heats, it contains the lattice energy U_g.

and

$$U_g = 287.2\nu \frac{z_+ z_-}{r_+ + r_-}\left(1 - \frac{0.345}{r_+ + r_-}\right) \qquad (3.4)$$

where ν = number of ions in a molecule of an ionic substance
z_+ and z_- = valencies
r_+ and r_- = radii of positive and negative ions.

In determining the heat of hydration it is possible to avoid calculating the lattice energy by using a more complicated cycle:



Here $_{KCl}\bar{Q}_f$ = heat of formation of crystalline potassium chloride [KCl] from potassium and chlorine taken in their standard state, i.e., in the form of solid metallic potassium [K] and gaseous molecular chlorine (Cl_2)

$-S_K$ = heat of sublimation of potassium with the formation of gaseous atomic potassium (K)

$\frac{1}{2} D_{Cl_2}$ = energy of dissociation of molecular chlorine into gaseous atoms (Cl)

$-I_{K^+}$ = energy corresponding to the first potential of ionization of potassium atom with the formation of gaseous potassium ion (K^+)

$+I_{Cl^-}$ = energy which is a measure of electron affinity of chlorine atom.

The remaining quantities have the same meaning as before. From this cycle it follows that

$$_{K^+}\bar{Q}_h + {}_{Cl^-}\bar{Q}_h = {}_{KCl}\bar{Q}_L + {}_{KCl}\bar{Q}_f + S_K + \frac{1}{2} D_{Cl_2} + I_{K^+} - I_{Cl^-} \qquad (3.5)$$

The heats of hydration have been determined for various compounds with the aid of the empirical methods discussed above. Some of the data obtained are given in Table 3.1.

TABLE 3.1

Heats of Hydration of Some Compounds

Compound	$\overline{Q}_h$, kcal/mole	Compound	$\overline{Q}_h$, kcal/mole	Compound	$\overline{Q}_h$, kcal/mole	Compound	$\overline{Q}_h$, kcal/mole
LiF	229	LiCl	210	LiBr	203	LiI	192
NaF	202	NaCl	185	NaBr	177	NaI	166
KF	182	KCl	165	KBr	156	KI	146
MgF_2	671	$MgCl_2$	635	$MgBr_2$	613	MgI_2	598
BaF_2	442	$BaCl_2$	406	$BaBr_2$	390	BaI_2	369
AlF_3	1430	$AlCl_3$	1378	$AlBr_3$	1354	AlI_3	1222
HF	366	HCl	349	HBr	341	HI	330
LiOH	208	NaOH	182	KOH	162	CsOH	148

3.2. HEATS OF HYDRATION OF INDIVIDUAL IONS

3.2.1. DEPENDENCE OF THE HEAT OF HYDRATION OF AN ION ON ITS PROPERTIES

The differences in the heats of hydration of electrolytes with a common ion, for example,

$$_{LiF}\overline{Q}_h - {}_{NaF}\overline{Q}_h \text{ and } {}_{LiCl}\overline{Q}_h - {}_{NaCl}\overline{Q}_h$$

or

$$_{NaF}\overline{Q}_h - {}_{NaCl}\overline{Q}_h \text{ and } {}_{KF}\overline{Q}_h - {}_{KCl}\overline{Q}_h$$

are closely similar (see Table 3.1). Hence, the heats of hydration of substances are additive, being composed of the heats of hydration of the constituent ions.

It can be seen from Table 3.1 that if the hydration energy of a cesium ion is taken to be equal to zero in the series of alkali metal hydroxides, then the values of the conditional hydration energies of cations will increase in the sequence indicated in Table 3.2.

In a similar way, using experimental data on the heats of hydration

TABLE 3.2

Variation of the Relative Heat of Hydration of Alkali Metal Hydroxides with Cationic Radius

Property	Ion			
	Cs^+	K^+	Na^+	Li^+
r (after Goldschmidt), Å	1.65	1.33	0.98	0.68
$\overline{Q}_h$, kcal/g-ion	0.00	14	34	60

TABLE 3.3

Variation of the Relative Heat of Hydration of Lithium Halides with Anionic Radius

Property	Ion			
	I^-	Br^-	Cl^-	F^-
r (after Goldschmidt), Å	2.20	1.96	1.81	1.33
$\overline{Q}_h$, kcal/g-ion	0.00	11	18	37

of lithium halides and putting ${}_{I^-}\overline{Q}_h = 0$, we compile a similar table for anions (Table 3.3). The relative values of the heats of hydration obtained indicate that the ionic size plays an important part in the process of hydration. The heats of hydration in a series of ions similar in their properties, as a rule, increase as their radii decrease.

TABLE 3.4

Variation of the Relative Heat of Hydration of Metal Halides with Cationic Charge

Property	Compound		
	LiCl	$MgCl_2$	$AgCl_3$
Valency of cation (z)	1	2	3
$\frac{1}{z}\overline{Q}_h$, kcal/g-eq	210	318	459

A comparison of the heats of hydration of metal halides having different valencies shows that the heat of hydration increases with increasing ionic charge (Table 3.4).

3.2.2. EXPERIMENTAL HYDRATION HEATS OF IONS

The heats of hydration of individual ions can be obtained from experimental values of the heats of hydration of substances by making certain assumptions as to what fraction of the total heat should be assigned to each of the ions. The heats of hydration of single ionic species thus obtained are called *experimental*, though they are all more or less arbitrary and depend on how close to reality the assumptions are. These heats therefore cannot be regarded as experimental and their comparison with calculated heats does not indicate the degree of reliability of the theoretical method employed.

We shall now discuss the principal methods of determining experimental heats of hydration.

An assumption has been made that since the valencies and crystallographic radii of the ions K^+ and F^- are equal ($r_{K^+} = r_{F^-} = 1.33$ Å) their heats of hydration must also be equal and can be determined simply by dividing in half the experimental heat of hydration of potassium fluoride. This assumption made by Bernal and Fowler does not take into account the fact that anions are more hydrophilic than cations, which means that the F^- ion requires a relatively larger fraction of the total heat of hydration.

A more realistic suggestion was made by Mishchenko in 1947, who assumed that the heats of hydration of the Cs^+ and I^- ions unequal in size are equal. The radius of the iodide ion is about 0.55 Å larger than that of the cesium ion. According to Mishchenko, the larger radius (compared with the cesium ion) and the associated decrease of the heat of hydration of the iodide ion must compensate for its excess hydrophilic capacity (as a negatively charged ion) and the consequent increase of the heat of hydration. Owing to the asymmetry of their dipoles molecules of water can come closer to anions than to cations. The asymmetry factor, as determined on the basis of various water-molecule models, lies in the range of 0.22-0.28 Å. The minimum possible distances between the centres of positive and negative ions of equal size and the centre of the water dipole must differ by twice this figure. The difference in the radii of the I^- and Cs^+ ions is 0.55 Å and provides mutual compensation of the effects of ionic size and hydrophilic capacity.

To resolve the total heats of hydration into individual values for the component ions extrapolation methods have been proposed, based on the dependence of heats of hydration on ionic radii. The method developed by Izmailov (1960) is of particular interest. It is known that the total heats of hydration of ions forming a given substance, as well as the differences in heats of hydration for like-charged ions can be determined quantitatively from experimental data. Since with increasing ionic radius r or with a decrease in its inverse $1/r$ heats of hydration tend toward zero, with increasing anionic radius the sum of the heats of hydration of the ions of electrolytes with the same cation M^+ but different anions A^- must tend to ${}_{M^+}\bar{Q}_h$, i.e.,

$$\lim ({}_{M^+}\bar{Q}_h + {}_{A^-}\bar{Q}_h)_{\frac{1}{r_{A^-}} \to 0} \to {}_{M^+}\bar{Q}_h$$

The difference in the heats of hydration of two cations will tend to the same limit if the radius of one of them (for example, the second) increases, i.e.,

$$\lim ({}_{M_1^+}\bar{Q}_h - {}_{M_2^+}\bar{Q}_h)_{\frac{1}{r_{M_2^+}} \to 0} \to {}_{M_1^+}\bar{Q}_h$$

Thus, if $({}_{M_1^+}\overline{Q}_h + {}_{A^-}\overline{Q}_h)$ or $({}_{M_1^+}\overline{Q}_h - {}_{M_2^+}\overline{Q}_h)$ is plotted against $1/r$ and the curves are extrapolated to $1/r_{A^-} = 0$ or $1/r_{M_2^+} = 0$, the intercept of the ordinate will correspond to ${}_{M_1^+}\overline{Q}_h$. The mean value of the sums and differences of the heats of hydration, i. e. the quantity

$$ {}_{M_1^+}\overline{Q}_h + \frac{{}_{A^-}\overline{Q}_h - {}_{M_2^+}\overline{Q}_h}{2} $$

must also tend in the limit to ${}_{M_1^+}\overline{Q}_h$ with increasing mean radius of cation M_2^+ and anion A^-, i.e., the quantity r_m determined from the equation

$$ \frac{1}{r_m} = \frac{1}{2}\left(\frac{1}{r_{M_2^+}} + \frac{1}{r_{A^-}}\right) $$

The determination of the hydration energy for a hydrogen ion by this method is illustrated in Fig. 3.1.

It should be noted that the heats and energies of hydration obtained by Mishchenko and Izmailov for individual ions are very close

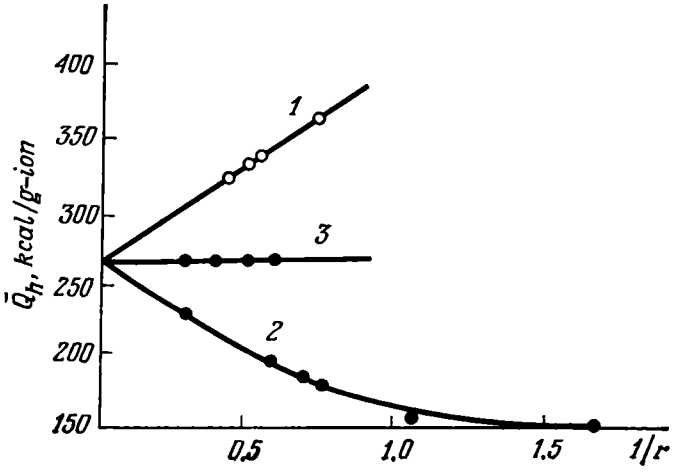


Fig. 3.1. Determination of the hydration energy of ions according to Izmailov: *1*—variation of the total hydration heat of acids as a function of anionic radius; *2*—the difference between the hydration heats of acids and their salts as a function of salt cation radius; *3*—the average sums and differences of the hydration heats of acids and their salts as a function of the mean radius of salt cation and anion

to each other, though their methods of resolving the total heats are based on different principles. Therefore the experimental individual heats of hydration as obtained by Mishchenko and Izmailov are considered to be the most reliable.

3.2.3. CALCULATION OF HEATS OF HYDRATION BY THE CONTINUUM METHOD

One of the first attempts to calculate theoretically the heats of hydration of individual ions was made by Born. His method of calculation is based on the assumption that the energy of solvation

(hydration) of an ion must equal the difference between its potential energies in vacuum U_V and in solution U_L:

$$U_S = U_V - U_L \tag{3.6}$$

The energy of an ion in vacuum is given by

$$U_V = \int_{q=0}^{q=ze} \frac{q}{r}\, dq = \frac{z^2e^2}{2r}$$

where ze = ionic charge
r = ionic radius.

The energy of an ion in a medium of dielectric constant D is

$$U_L = \int_{q=0}^{q=ze} \frac{q}{rD}\, dq = \frac{z^2e^2}{2rD}$$

and the solvation energy in terms of a gram-ion is

$$U_S = N_A \frac{z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \tag{3.7}$$

Since the heat and energy of hydration are interrelated by the Gibbs-Helmholtz equation (I.32), which in this particular case, i.e., for $U_S = -\Delta G_S$, may be rewritten as

$$U_S = \bar{Q}_S + T\frac{\partial U_S}{\partial T} \tag{3.8}$$

it follows that

$$Q_S = N_A \frac{z^2e^2}{2r}\left[1 - \frac{1}{D} - \frac{T}{D^2}\left(\frac{\partial D}{\partial T}\right)\right] \tag{3.9}$$

Thus, according to Born, the solvation energy of an ion is determined by its charge and dimensions as well as by the dielectric constant of the solvent. Equations (3.7) and (3.9) can be applied to any solution provided that its dielectric constant is known.

Since electrolytes dissociate owing to the energy of solvation, it should be expected, if Born's ideas are accepted, that the dissociating power of the solvent is in direct proportion to its dielectric constant. This regularity was established by Walden (1903) even before Born's solvation theory appeared. Walden formulated the following empirical rule (known as *Walden's rule*) for the tetrasubstituted series of ammonia:

$$D\sqrt[3]{V_\alpha} = \text{const} \tag{3.10}$$

where V_α is the dilution required to attain a definite degree of dissociation α equal for all solutions compared. The data obtained at $\alpha = 0.83$ are presented in Table 3.5.

TABLE 3.5

Relation Between the Dielectric Constant and Dissociating Power of Solvents (after Walden)

Solvent	D	$V_{\alpha=0.83}$	$D\sqrt[3]{V_{\alpha=0.83}}$
Water	81.7	32	254
Nitromethane	40	200	234
Methanol	32.5	400	240
Acetylacetone	26	1000	260
Anisaldehyde	15.5	3100	226

Walden's rule however is of limited applicability, a circumstance noted first by Pisarzhevsky.

To use Born's equation for calculations it is necessary to know, along with the dielectric constant of the solution, the valency and radius of the ion concerned. The valencies of ions are known, and their radii are taken by Born to be equal to crystallographic radii. The latter are effective ionic radii and depend on the type of crystal lattice. The use of effective radii in place of ionic radii in solutions may lead to errors in calculations. Another drawback of the Born theory is that the dielectric constant of a solution is assumed to be identical with that of a pure solvent, which contradicts experimental data. If we calculate the heats of hydration for sodium, potassium, fluoride and chloride ions on the basis of these assumptions, the following series will result:

Ion	Na^+	K^+	F^-	Cl^-
Q_h, kcal/g-ion . .	166	123	123	90

A comparison of the heats of hydration of the compounds NaF, NaCl, KF and KCl calculated from the Born equation with their experimental values (see Table 3.1) reveals that the theoretical values are higher than the experimental data, though Born's equation yields a qualitatively correct relation between the energies (heats) of solvation and the properties of ions. For instance, in full accord with experiment, the heats of hydration become greater as fluoride or sodium ions are substituted for chloride or potassium ions, respectively, in the molecule, i.e., as the ionic radius decreases.

An attempt to refine Born's equation was made by Webb, who introduced corrections for a fall in the dielectric constant of a solution in the immediate neighbourhood of the ion and for the work of compressing the solvent during the introduction of an electrolyte (this phenomenon is known as *electrostriction*). In making these corrections Webb proceeded from the dependence of the dielectric constant of a dielectric on the properties of its constituent particles and their behaviour in an electric field.

It is known that with a constant charge density on the plates of a parallel-plate condenser the field strength between them is found to be greater in vacuum, ψ'_V, than in a dielectric, ψ'_D. The ratio

$$\frac{\psi'_V}{\psi'_D} = D \tag{3.11}$$

is called the *dielectric constant* D of a substance, assuming that in vacuum D is equal to unity.

Equation (3.11) implies that part of the charges on the capacitor plates are compensated for by the charges of the dielectric. If the molecules of the dielectric are polar, i.e., the centres of gravity of the positive and negative charges do not coincide, then such molecules possess a *permanent dipole moment* μ_p. The *dipole moment* is here defined as the product of any one of the dipole charges, q, and the distance between their centres of gravity, l:

$$\mu = ql \tag{3.12}$$

The charge q is a multiple of the electron charge (4.803×10^{-10} esu), and l is equal to several angstroms (1 Å $= 10^{-8}$ cm). Consequently, the dipole moment must be of the order of 10^{-18}. The magnitude of the dipole moment equal to 1×10^{-18} is called the *debye* (D). Under the influence of an electric field polar molecules are oriented so that their positive ends are directed toward the negative capacitor plate, and their negative ends toward the positive plate, thereby compensating part of the capacitor charges. The degree of molecular orientation increases with increasing field strength and for large fields, when all the molecules of the dielectric become oriented, its response to the electric field will not differ formally from that of vacuum. Under these conditions a state is reached which is called *dielectric saturation*, and the dielectric constant of the substance approaches unity. The orienting effect of the field is counteracted by the thermal motion of particles. With equal field strengths, the higher the temperature the lower is the degree of orientation and the later will the state of dielectric saturation be attained (i.e., at increased field strength).

It should be kept in mind that the particles of dielectrics having no permanent dipole are capable of altering their shape under the influence of an external field, as a result of which they may acquire a dipole moment. The moment due to an electric field is called the *induced dipole moment* μ_{in}. The displacement of charges in a dielectric particle giving rise to an induced dipole will always reduce the field strength irrespective of the temperature. For not-too-large fields the magnitude of an induced dipole is proportional to the field strength:

$$\mu_{in} = \alpha\psi' \tag{3.13}$$

where α is the *polarizability*.

The dielectric constant as a macroscopic characteristic of a substance is related with the microscopic properties of the particles making up a given substance, namely, with their dipole moments and polarizability. Various equations have been proposed to describe this relation. One of the earliest and most widely used is the Debye equation

$$\frac{D-1}{D+2}\cdot\frac{M}{d}=\frac{4}{3}\pi N_A\frac{\bar{\mu}_p^2}{3kT}+\frac{4}{3}\pi N_A\alpha \qquad (3.14)$$

where M = molecular weight
d = density of the substance
$\bar{\mu}_p$ = component of the permanent dipole moment in the direction of the field.

If an electrolyte is introduced into a pure solvent of dielectric constant D_0, part of the solvent molecules will orient themselves in an electric field set up by the ion charges of the electrolyte. The dielectric constant of the solvent must then decrease because some of its molecules will be oriented around the ions and become passive in respect of the external field. The dielectric constant of the solution is therefore lower than that of the initial solvent. The lowest value of the dielectric constant is observed in the vicinity of an ion. In the case of ions of different size but equal charge, the smaller the ionic radius, the more pronounced is the depression of the dielectric constant. Accordingly, Webb introduces into the Born equation the values of dielectric constant corresponding to each radius (D_r), which is always lower than the dielectric constant of a pure solvent. The second effect taken into account by Webb is associated with the phenomenon of electrostriction, i.e., compression upon dissolution. As a result of electrostriction the volume of the solution becomes smaller than the sum of the volumes of the pure solvent and solute. A certain amount of energy is required for the work of compression. Both these effects being taken into account, the energy and heat of hydration calculated from the Born-Webb formula diminish and approach experimental values. In the Webb theory, however, the solvent is still regarded as a continuous medium and neither the structure of its molecules nor the constitution of the liquid is reckoned with. But these properties may be more significant than the value of dielectric constant. For example, comparing the data of Tables 3.1 and 3.6, one can see that in alcohols, the dielectric constant of which is lower than that of water, the heats of solvation are approximately the same as for water. In some cases they are even higher than the corresponding heats of hydration.

Thus, the assumption of the exclusive role of dielectric constant in the solvation and dissociation of electrolytes does not agree quantitatively with experimental facts. To work out a correct idea of these phenomena, one must consider the interaction between the

TABLE 3.6

Solvation Heats of Alkali Metal Halides in Nonaqueous Solvents

Solvent	LiCl	NaCl	NaBr	NaI	KI
CH_3OH ($D=32.6$)	216	189	179	170	—
C_2H_5OH ($D=25.2$)	217	—	178	169	148

solute and the solvent, i.e., following Mendeleyev, one must view the process of electrolytic dissociation not only as the decomposition of the initial particles but also as the formation of new ones. Kablukov was the first to suggest combining Mendeleyev's hydrate theory and the Arrhenius theory of electrolytic dissociation. As far back as 1891 he noted the presence of interaction between the molecules of the solvent and those of the solute, as a result of which the bonds in the electrolyte molecules are disrupted and complexes are formed between individual ions and solvent molecules. This phenomenon was later given the name of solvation in general, or hydration in the particular case of aqueous solutions.

3.2.4. MODELISTIC METHODS OF CALCULATING HYDRATION ENERGY

Van Arkel and de Boer's Method. To abandon the continuum theory (i.e., the concept of a solvent as a certain continuous and homogeneous medium) and consider the interaction between electrolyte ions and solvent molecules, one must have at his disposal data on the structure and properties of the molecules of a solvent and on the forces responsible for the process of solvation (ion-solvent interaction).

One of the first model methods of calculating the energy of hydration was that proposed by van Arkel and de Boer. They suggested separating the energy of hydration into two components, one corresponding to the energy of formation of the first hydrate shell and the other to the subsequent process of hydration. The energy of hydration was computed on the basis of the following cycle:

1. The number of molecules of water (n) required for the formation of the primary shell of hydration is evaporated (in agreement with the most usual coordination numbers n is taken as equal to 4, 6 or 8). The amount of energy spent on this process is $n\lambda$, where λ is the latent heat of evaporation of one molecule of water.

2. The evaporated n molecules of water react with an ion in the gaseous phase to form a hydrated ion of radius r_a; the energy γ

evolved in this process is composed of the energy of ion-dipole interaction, the energy of attraction and repulsion of dipoles, the energy of producing induced dipoles and finally the Born repulsive energy.

3. The resulting complex of radius r_a ($r_a = r + 2r_w$, where r is the crystallographic ionic radius, and r_w the radius of a water molecule) is introduced into the solution. The energy evolved is calculated from the Born-Webb formula:

$$\frac{z^2e^2}{2r_a}\left(1-\frac{1}{D_{r_a}}\right) \qquad (3.15)$$

The heat of hydration in terms of a gram-ion is the sum of all the partial energy effects, i.e.,

$$U_h = N_A\left[-n\lambda+\gamma+\frac{z^2e^2}{2r_a}\left(1-\frac{1}{D_{r_a}}\right)\right] \qquad (3.16)$$

This formula provides a better agreement with experiment than Born's formula. The van Arkel-de Boer method differs from the Born method in that the process of hydration is divided into two steps. The energy of formation of the primary shell of hydration is computed on the basis of the interaction between the gaseous ion and the polar water molecules, i.e., the interaction taking place outside the liquid phase. This method of calculation permits one to take into account the properties of individual water molecules (their dipole moments, polarizability, etc.). Therefore, in considering the process of formation of the primary hydration shell, where these properties acquire special significance, it is possible to discard the concept of water as just a medium of definite dielectric constant. Since in the second step of the cycle an ion, which is already partly hydrated and has a radius much larger than the radius of the initial ion, is introduced into water, an identical error in the determination of the radius of the initial ion will be of less significance here. The perturbations caused by the introduction of such a hydrated ion into the water will be smaller and the concept of water as a continuum of definite dielectric constant, and hence the use of formula (3.15), appear to be more justified than in the Born method. Van Arkel and de Boer view the water molecule as a sphere with a radius of 1.25 Å and a dipole moment equal to 1.85 debyes.

The van Arkel-de Boer method has been developed and refined, particularly by Mishchenko and his associates. In his works Mishchenko takes into account the asymmetry of a water dipole, i.e., the fact that the positive charge of the molecules of water is situated nearer its periphery than the negative charge. This modified model of the water molecule made it possible to consider the difference in the hydrophilic capacity of anions and cations of equal dimensions and valencies. Further, Mishchenko took into account some additional effects that had not been reckoned with by previous investigators, for example, the thermal motion of molecules in the hydrate

shell, and dispersion forces. All this made calculations more accurate and rigorous.

The Bernal-Fowler Method and Its Modifications. Another trend in theoretical work on heats of hydration was initiated by the investigations of Bernal and Fowler concerning the nature of water and ice (1935). Water displays a number of anomalies. Some of its properties prove to be extremal at a definite temperature. Water has a maximum density at 4°C and the lowest heat capacity at 34.5°C, etc. The density of water at a temperature close to the freezing point is higher than that of ice, the ratio $d^{4°C}_{H_2O}/d^{4°C}_{[H_2O]}$ being equal to 1.1. Attempts were made to explain these anomalous properties of water as follows. Water molecules exist in the form of associates of the type $(H_2O)_n$, where n may be any integer from 1 to 18. With a change of temperature (or pressure) the association equilibrium is disturbed, the relative fraction of each of these complexes is altered, and as a consequence the properties of the water are changed. Some additional considerations have recently been put forward in favour of this theory, but the concepts of the quasi-crystalline structure of water underlying the theory of Bernal and Fowler are now considered as more probable, for which reason we shall discuss them in more detail.

The polar nature of the water molecule and its triangular structure cause each molecule to exert an orienting effect on its nearest neighbours. The angle $O\begin{smallmatrix}H\\ \diagup\\ \diagdown\\ H\end{smallmatrix}$ in the water molecule is close to the tetrahedral angle and therefore the most probable structure of water is a tetrahedral one. X-ray and other techniques indicate that at ordinary pressures and near-freezing temperatures a quasi-crystalline structure similar to the tridymite structure predominates. With increasing temperature the tridymite structure is replaced by an irregular analogue of the quartz structure which has a higher density than tridymite. The maximum density of water at 4°C is attributed to the superposition of the packing effect (associated with transformation from tridymite to quartz) on the effect of thermal expansion. A further rise of temperature disturbs the ordered arrangement of the liquid particles and converts the water to an amorphous state. At near-critical temperatures water does not reveal any signs of quasi-crystallinity. However, under ordinary conditions in which the heat of hydration is usually determined, the quasi-crystalline structure must be of great importance to the energetics of the hydration process. This idea, first suggested by Bernal and Fowler, was later used by them and by many other authors to compute heats of hydration.

Thus, for example, Eley and Evans (1938) used a cycle consisting of the following steps:

1. The tetrahedral group of water is taken out of the solution into the gas phase. This is achieved at the expense of the energy of interaction L_t between the tetrahedron molecules and the surrounding liquid. The removal of the group leaves a cavity in the solution.

2. The group is then split in the gas phase into five free water molecules. The disruption of the bonds holding together these molecules requires energy β.

3. Four out of the five water molecules formed are joined to the free gas ion with the release of energy π associated with the interaction between the water dipoles and the ion.

4. Now the group, in which one water molecule is replaced by an ion, is transferred back into the cavity formed in step 1. This process may involve evolution or absorption of energy γ as a result of the reorientation of the water molecules in the layer adjacent to the group. This is caused by a change in the size of the group and by the reorientation of its molecules as well as by the interaction between the group and the surrounding molecules. This interaction is now of a different nature due to the appearance of a net charge.

5. The water molecule is returned to the solution with the liberation of energy λ.

According to Eley and Evans the hydration energy is determined from the following formula:

$$U_h = N_A (- L_t - \beta + \pi - \gamma + \lambda) \qquad (3.17)$$

Some of the quantities in Eq. (3.17) are independent of the nature of the ion and can be computed in advance. For instance, one can calculate the energy of dissociation β of the tetrahedron into five free molecules. If all the coulombic effects are taken into account, this energy is 21 kcal/mole after Eley and Evans. The heat of condensation $N_A\lambda$ of one gram-molecule of water is equal to 10 kcal. The value of π is determined in the same manner as β, with account taken of coulombic forces of interaction between the water dipoles and between these dipoles and an ion of a given charge and radius. The values of γ and L_t are not determined separately, but their difference can be computed. In calculations, the difference in the dimensions of the formed and initial tetrahedra is ignored. When one water molecule is replaced by an ion in the tetrahedron, four molecules of water are reoriented around the ion introduced. The forces of interaction between the reoriented water molecules and the water molecules which surround them but are not part of the tetrahedron will be different from the forces observed for the original group. The change of the interaction energy is denoted by δ. When the charged tetrahedron is transferred back into the solution, an energy is produced that is given by the Born formula:

$$\frac{z^2e^2}{2r_a}\left(1-\frac{1}{D}\right)$$

and so

$$\gamma - L_t = \frac{z^2e^2}{2r_a}\left(1-\frac{1}{D}\right) - \delta$$

The overall value of hydration energy for a gram-ion is

$$U_h = N_A \frac{z^2e^2}{2r_a}\left(1-\frac{1}{D}\right) + N_A\pi - N_A\delta - 21 + 10 \qquad (3.18)$$

For negative univalent ions $N_A\delta = 20$ kcal, and for positive univalent ions $N_A\delta = 8$ kcal, i.e., for A^- anions

$$_{A^-}U_h = N_A \frac{e^2}{2r_a}\left(1-\frac{1}{D}\right) + N_A\pi - 31 \qquad (3.19)$$

and for M^+ cations

$$_{M^+}U_h = N_A \frac{e^2}{2r_a}\left(1-\frac{1}{D}\right) + N_A\pi - 19 \qquad (3.20)$$

The Eley-Evans method assumes the hydrophilic capacity of cations and anions to be equal and takes into account only the coulombic forces of interaction between electrolyte ions and water dipoles. Besides, the quantitative treatment in their method is based solely on the coordination number 4, which narrows the range of its applicability.

3.2.5. COMPARISON OF THE HYDRATION ENERGIES OF INDIVIDUAL IONS. CHEMICAL AND REAL HYDRATION ENERGIES

Now that we are acquainted with the principal computing techniques employed in the study of the energetics of the hydration process, it is interesting to compare the results obtained with the aid of these methods. This comparison helps, in the first place, to judge about the values of heats and energies of hydration and, secondly, to see how well the data of various authors agree. The values of the heats and energies of hydration obtained by the methods described above are presented in Tables 3.7 and 3.8, respectively. The results of calculations made by other methods are also included for comparison. In the Fajans method, use is made of cycles involving the application of hydrogen and potassium-amalgam electrodes, and the heats of hydration are calculated accordingly for the proton and the potassium ion. Combining the thus obtained values with experimental heats of hydration of electrolytes enables one to find heats of hydration for any other ions. Though in this case use is made of the so-called Ostwald "absolute" scale of potentials, which cannot be regarded as scientifically founded, the data obtained by Fajans present certain interest as the first results of theoretical calculation of hydration heats.

In using Tables 3.7 and 3.8 one should remember that not all authors made strict distinction between heats and energies of hydration. The values of hydration heats therefore included terms corresponding to changes in free energy, and those of hydration energies

TABLE 3.7

Chemical Heats of Hydration for Individual Ions

Ion	r, Å	$\overline{Q}_{h\,(ch)} = -\Delta H_{h\,(ch)}$, kcal/g-ion					
		Fajans	Van Arkel and de Boer	Bernal and Fowler	Eley and Evans	A group of authors	Izmailov
Ag^+	1.13	—	—	—	104	117	—
Al^{3+}	0.57	—	—	—	1010	1125	—
Br^-	1.96	73	—	63	52	76	77
Ca^{2+}	1.04	—	—	410	428	386	—
Cd^{2+}	0.99	—	—	—	433	439	—
Cl^-	1.81	83	—	67	59	84	88
Co^{2+}	0.78	—	—	—	488	499	—
Cs^+	1.65	—	—	79	73	67	—
Cu^{2+}	0.80	—	—	—	526	509	—
F^-	1.33	123	—	94	91	116	—
Fe^{2+}	0.80	—	—	—	485	467	—
Ga^{3+}	0.62	—	—	—	—	1131	—
H^+	0.00	255	259	—	—	—	—
Hg^{2+}	1.12	—	—	—	412	443	—
I^-	2.20	63	—	48	45	67	66
K^+	1.33	77	—	92	90	81	78
La^{3+}	1.04	—	—	—	708	796	—
Li^+	0.68	131	161	131	133	127	125
Mg^{2+}	0.74	—	—	495	501	467	—
Mn^{2+}	0.91	—	—	—	461	449	—
Na^+	0.98	97	97	116	115	101	98
Ni^{2+}	0.74	—	—	—	499	511	—
Pb^{2+}	1.26	—	—	—	—	362	—
Rb^+	1.49	73	—	87	81	75	—
Zn^{2+}	0.83	—	—	—	485	496	—

included thermal effects. The most exhaustive distinction between heats and energies of hydration was drawn by Eley and Evans, Izmailov and a group of authors including Vasilyev, Zolotarev, Kapustinsky, Mishchenko, Podgornaya, and Yatsimirsky (1960).

As first noted by Lange and Mishchenko (1930), all the known methods of calculating ionic heats and energies of hydration ignore the electrical work done by an ion in traversing the vacuum-solution interface. In calculations, account is taken of only the ion-solvent interaction; the calculated energies and heats of hydration thus obtained were named by these authors the chemical energies and heats of hydration. If the charge of a gram-ion is zF and the potential

TABLE 3.8

Chemical Energies of Hydration for Individual Ions

Ion	r, Å	$U_{h\,(ch)} = -\Delta G_{h\,(ch)}$, kcal/g-ion		
		Born and Webb	A group of authors	Izmailov
Ag^+	1.13	95.5	113	112
Al^{3+}	0.57	—	1094	—
Br^-	1.96	66	72	68.0
Ca^{2+}	1.04	—	373	372.4
Cd^{2+}	0.99	—	425	430.0
Cl^-	1.81	70	79	74.0
Co^{2+}	0.78	—	480	—
Cs^+	1.65	71.5	66	64.0
Cu^{2+}	0.80	—	491	—
F^-	1.33	87	107	—
Fe^{2+}	0.80	—	448	—
H^+	0.00	250	—	258.0
Hg^{2+}	1.12	—	431	—
I^-	2.20	61	64	59
K^+	1.33	82	79	78
La^{3+}	1.04	—	774	—
Li^+	0.68	—	121	117
Na^+	0.98	99	97	96
Ni^{2+}	0.74	—	491	—
Pb^{2+}	1.26	—	353	—
Rb^+	1.49	77	74	74.4
Zn^{2+}	0.83	—	479	492.0

jump across the vacuum-solvent interface is represented by χ, then the electrical work involved in traversing this interface will be

$$zF\chi \tag{3.21}$$

At the same time the experimental data on the heats and energies of hydration of ions include electrical terms. It should be noted that the presence of a potential jump χ and the associated electrical energy of ion transfer does not affect the energy of hydration of an electrolyte as a whole since the law of electroneutrality holds for any electrolyte:

$$\Sigma \nu_i z_i = 0$$

and, consequently,

$$\Sigma \nu_i z_i F\chi = 0$$

The heats and energies of hydration which include the energy change on passage of an ion across the potential difference χ were named, respectively, the *real heats* and *energies of hydration* as suggested by Lange and Mishchenko. The real and chemical energies of hydration are connected by the following relation

$$\Delta G_{h(r)} = \Delta G_{h\,(ch)} \pm zF\chi \tag{3.22}$$

An analogous equation [1] is used to interrelate the real and chemical heats of hydration:

$$\Delta H_{h(r)} = \Delta H_{h(ch)} \pm zF\chi \qquad (3.23)$$

The chemical heats ΔH_h and chemical energies ΔG_h are given in Tables 3.7 and 3.8.

A comparison of the values of chemical heats of hydration ΔH_h and chemical energies of hydration ΔG_h shows that the difference between them is not great. For each particular ion the difference between the heat and the energy of hydration is smaller than that between the values of ΔH_h or ΔG_h obtained by different authors. Since

$$\Delta H_h = \Delta G_h + T\Delta S_h$$

the closeness of the values of ΔH_h and ΔG_h for a given electrolyte implies that the entropies of hydration ΔS_h are small.

TABLE 3.9

Real Energies of Hydration for Individual Ions

Ion	r, Å	$U_{h(r)} = -\Delta G_{h(r)}$, kcal/g-ion		
		Klein and Lange	Mishchenko	Randles
Ag^+	1.13	124	114	—
Br^-	1.96	—	64.3	64.9
Ca^{2+}	1.04	—	378.3	—
Cd^{2+}	0.99	439	433	—
Cl^-	1.81	—	70	70.7
Cs^+	1.65	—	68.3	67.8
Cu^{2+}	0.80	519	—	—
F^-	1.33	—	98.2	99.1
Fe^{2+}	0.80	475	—	—
H^+	0.00	—	261	260.5
Hg^{2+}	1.12	459	—	—
I^-	2.20	—	56.2	57.2
K^+	1.33	92	81.2	80.6
Li^+	0.68	127	121.4	122.1
Mg^{2+}	0.74	425	458.6	—
Mn^{2+}	0.91	452	—	—
Na^+	0.98	101	98.8	98.2
Ni^{2+}	0.74	501	—	—
Rb^+	1.49	83	77.5	75.5
Zn^{2+}	0.83	491	487	—

A method for calculating real energies of hydration with the use of experimental data on the electromotive force was first indicated

[1] In Eqs. (3.22) and (3.23) the plus sign refers to anions, and the minus sign to cations.

by Frumkin and subsequently employed by a number of authors. Table 3.9 lists the values of real hydration energy for some ions obtained by various investigators.

For each particular electrolyte the sum of the chemical heats or chemical energies of hydration of ions must equal the sum of the real heats or real energies of hydration of the same ions and express the overall heat or energy of hydration of the substance in question. A comparison of the data of Table 3.1 with those presented in Tables 3.7, 3.8 and 3.9 will show that this condition is not observed with sufficient consistency. The discrepancy between theory and experiment is largely due to the fact that different authors used different thermochemical data for calculations. Recent results show better agreement. This permits one to consider the heats of hydration ΔH_h and the energies of hydration ΔG_h as more or less reliable characteristics of the energy state of ions in aqueous solutions.

The differences in the chemical and real energies of hydration of ions make it possible to estimate the value of the potential difference χ across the vacuum-solution interface. According to Frumkin (in his opinion the data of Randles (1956) on real energies of hydration and Izmailov's data on chemical energies of hydration are the most reliable), the value of potential difference χ^{H_2O} must be close to ± 0.1 V.

3.2.6. ENTROPY OF SOLVATION

As shown above, the dissolution of substances dissociating into ions increases the degree of ordering of a solvent. This is manifested, for instance, in the decrease of the dielectric constant of the solution with increasing electrolyte concentration. The orderliness is a result of the interaction between solvent particles and electrolyte ions and must increase with the heat of solvation. The entropy characterizes the degree of disorder in a system. The entropy of solvation is therefore always negative; the more exothermic is the reaction of solvation, the higher is the entropy in absolute value.

The standard entropy of solvation is defined as the difference in the entropies of an ion in solution and in vacuum:

$$\Delta S_S^0 = S_L^0 - S_V^0$$

The *reference* or *standard state* is taken to be a gas at 25°C and a pressure of 1 atm or a solution at 25°C and unit ionic activity. Experiment can only yield the total entropy of solvation of an electrolyte. To compute the solvation entropy of individual ions, one has to resort to various assumptions as was done in calculating individual heats of solvation.

Table 3.10 gives the values of individual entropies of hydration obtained by Eley and Evans.

TABLE 3.10

Entropies of Hydration of Individual Ions

Ion	r, Å	$-\Delta S_h$, cal/g-ion·°C	Ion	r, Å	$-\Delta S_h$, cal/g-ion·°C
Li^+	0.86	34.7	Al^{3+}	0.57	104.1
Na^+	0.98	28.3	F^-	1.33	35.2
K^+	1.33	21.8	Cl^-	1.81	24.2
Cd^{2+}	0.99	63.8	Br^-	1.96	15.4
Fe^{2+}	0.80	69.7	I^-	2.20	8.8

From Table 3.10 it follows that the entropies of hydration are small in magnitude and increase with decreasing ionic radius and increasing ionic charge.

3.2.7. HYDRATION NUMBERS

As a result of the process of solvation, the solution must contain ions with a solvent sheath rather than free ions. Bockris and Conway (1954) distinguish between the primary and the secondary solvent sheath (or shell). The former includes solvent molecules strongly bound with an ion and moving together with it, and the latter all the water molecules the state of which is different from that of water molecules in a pure solvent. For many electrochemical processes it is important to know how many solvent molecules are inside the primary solvent shell and could therefore be considered participants in the solvation of the ion. This number is termed the *solvation number* n_S, or *hydration number* n_h when water is the solvent. These are relative values which provide only approximate information as to the number of water molecules contained in the internal layer. Different methods yield widely differing hydration numbers. In the Ulich method the formation of the primary hydrate shell is assumed to be similar to the freezing of water. This conception is shared by many other authors. Eley and Evans, for example, compare the solvent layer with a microscopic iceberg formed around a solute particle. Since the decrease of entropy on freezing of water is 6 cal/mole·deg, the hydration number is

$$n_h = -\frac{\Delta S_h^0}{6} \tag{3.24}$$

Another method is based on the variation of the dielectric constant of the solution with electrolyte concentration. This variation can be described by the equation

$$D = D_0 - (\delta_+ + \delta_-)\, c \tag{3.25}$$

where D = dielectric constant of solution
D_0 = dielectric constant of solvent
δ_+ and δ_- = positive coefficients for cations and anions.

Assuming that the solvent molecules forming the primary shell of hydration around the ion do not participate in the processes of orientation and polarization, i.e., in the formation of the dielectric constant, we may write:

$$D = D_0 - \frac{n_h M_w D_0}{1000} c = D_0 - (\delta_+ + \delta_-) c \qquad (3.26)$$

where n_h = minimum number of molecules in the primary hydration sheath
M_w = molecular weight of water.

The sum of the coefficients δ_+ and δ_- is found experimentally for the range of concentrations where the linear dependence of dielectric constant on concentration is preserved. This sum is resolved into its components in accordance with the nature of the influence of cations and anions on the rotational motion of the water molecules in the primary shell of hydration.

Hydration numbers can also be determined by measuring the compressibility of the water and the solution. The compressibility for the first layer must be lower than for the remaining part of the solvent. Having determined the compressibilities by the ultrasonic method (from the velocity of propagation of ultrasonic waves in the solution) and assuming that the compressibility of the primary shell of hydration is zero and that the I^- and Br^- ions are completely devoid of a primary hydration shell, Passynsky computed hydration numbers for a number of ions.

A comparison of the hydration numbers obtained by the three methods indicated above is made in Table 3.11. Though the results

TABLE 3.11

The Hydration Numbers of Individual Ions Determined by Different Methods

Method	Ion									
	H^+	Li^+	Na^+	K^+	Mg^{2+}	Al^{3+}	F^-	Cl^-	Br^-	I^-
By Eq. (3.24)	5	5	4	3	13	21	5	3	2	1
By Eq. (3.26)	10.5	6	4	4	16.5	—	—	—	—	—
After Passynsky	1±2	5-6	6-7	6-7	16	31	2	1	0	0

obtained by these methods are far from uniform, they all indicate that hydration numbers increase with decreasing ionic radius and increasing ionic charge.

3.2.8. HEATS AND ENERGIES OF SOLVATION OF ELECTROLYTES IN NONAQUEOUS SOLUTIONS

The energetics of the process of solvation of electrolytes for nonaqueous solvents has been little studied. There is only a limited amount of reliable data, including the values of heats and energies of solvation for a number of electrolytes obtained by Mishchenko and Izmailov.

The theory of calculation of the solvation energy for individual ions in the case of nonaqueous solutions has not yet been worked out. Attempts to apply modelistic methods similar to those used for computing hydration energies have failed. It appears that individual energies of solvation calculated in this way are entirely incompatible with experimental total solvation energies. In practice the overall values of solvation energy can be resolved into separate values for the component ions by using the semi-empirical methods of Mishchenko and Izmailov.

The Mishchenko method is based on the assumption that in all solvents anions are solvated stronger than cations of equal radius and valency. This is Mishchenko's principle of constancy of the ratio of solvation energies (or heats) of anions and cations for all solvents. It is known that the higher hydrophilic capacity of anions compared with cations is due to the asymmetry in the structure of water molecules. The assumption made by Mishchenko may be valid only for solvents the molecules of which have a structure similar to that of water molecules.

Izmailov's method based on the experimentally established decrease of solvation energy with increase of ionic radius seems to be more substantiated. True, in the case of nonaqueous solutions both these methods yield close values of empirical individual energies and heats of solvation. This can be seen from Table 3.12 which presents empirical chemical heats and energies of hydration of individual ions for some solvents as determined by the methods of Mishchenko and Izmailov.

From Table 3.12 it is seen that the chemical energy of ion solvation decreases in the sequence: water, methanol, ethanol. For liquid ammonia, the energies of solvation of cations appear to be higher, and those of anions lower, than the respective energies of hydration; the reverse is true for formic acid. A comparison of the heats and energies of solvation obtained by one and the same method reveals that the difference $\Delta H_S - \Delta G_S$ increases in the order: water, methanol, ethanol. This increase is associated with the decrease of solvation energy and the increase of solvation heat in the same order. Since

$$\Delta H - \Delta G = \Delta TS$$

TABLE 3.12

Chemical Heats and Chemical Energies of Solvation for Individual Ions

Solvent	Heat and energy of solvation*	Ions of radius, Å										
		Ag^+	Br^-	Cd^{2+}	Cl^-	Cs^+	H^+	I^-	K^+	Li^+	Na^+	Zn^{2+}
		1.13	1 96	0.99	1.81	1.65	0.00	2.20	1.33	0.68	0.98	0.83
Water	$-\Delta H_S$ (I)	—	77.0	—	88	—	—	66.0	78.0	125.0	98.0	—
	$-\Delta G_S$ (I)	—	71.0	—	76.1	—	—	62.0	75.4	115.0	93.0	—
	$-\Delta G_S$ (II)	112.0	68.0	430.4	74.0	64.0	258.0	59.4	78.0	117.0	96.0	492.0
Liquid ammonia	$-\Delta G_S$ (II)	132	62.8	546	65.5	65.6	281.0	57.0	79.4	124.0	99.0	536.0
Methyl alcohol	$-\Delta H_S$ (I)	—	79.0	—	84.0	—	—	70.0	—	127.0	100.0	—
	$-\Delta G_S$ (I)	—	69.4	—	73.4	—	—	61.8	73.6	114.0	90.7	—
	$-\Delta G_S$(II)	108.0	67.0	417.0	71.0	60.4	253.0	59.6	76.0	116.0	93.0	481.0
Ethyl alcohol	$-\Delta H_S$ (I)	—	78.0	—	90.0	—	—	69.0	79.0	127.0	99.0	—
	$-\Delta G_S$ (I)	—	86.1	—	72.2	—	—	60.0	71.7	112.0	88.4	—
	$-\Delta G_S$ (II)	108.0	66.2	413.0	71.3	—	252.0	58.5	73.2	115.0	90.0	473.5
Formic acid	$-\Delta G_S$ (II)	120.8	—	410.4	78.3	65.0	246.0	—	73.9	116.0	99.5	488.3

* The Roman figures I and II enclosed in parentheses stand for the Mishchenko and Izmailov methods, respectively.

the regularity observed should be attributed to the greater variation of the solvation entropy of alcohols. Since the entropy of solvation is always negative, the effect of ordering must be stronger in alcohols than in water when solvation sheaths are formed around the ions.

It follows from Table 3.12 that the heats (and especially the energies) of solvation vary only slightly from solvent to solvent, though their dielectric constants differ sharply. Considering the lack of well-defined dependence of solvation energies on the dielectric constant and molecular structure of a solvent, Izmailov came to the conclusion that the process of solvation must be based on factors other than those adopted by the existing modelistic methods of calculation. In this connection, mention must be made of the theory of electrolytic solutions developed by Samoilov (1957) and based on Frenkel's molecular-kinetic theory of liquids and Bernal and Fowler's theory of water structure. Following Mishchenko, Samoilov defines solvation as the sum of all the changes in the state of the solution caused by the electrolyte ions that appear in it. According to Samoilov, these changes are caused by the interaction of electrolyte ions with their immediate environment and also by the influence of the ions upon further removed water layers. Long-range interaction is based on the polarization of water layers under the influence of an electric field. Short-range interaction is associated with the change of the nature of thermal motion of solvent molecules adjacent to the ion. It manifests itself mainly in a change of translational motion, i.e., in a change of the conditions of the jumpwise shift of molecules from one position of equilibrium to the next. In this case the ions influence mainly the activation energy of translational motion, U_a. This effect is characterized by the quantity ΔU_a, i.e., the change of activation energy as a result of the appearance of electrolyte ions in the solvent. The quantity ΔU_a depends on the nature of ions; it may be either positive or negative. In the former case the introduction of ions hampers the exchange between the water molecules adjoining them and those of the next layer, as compared with exchange in pure water (so-called *positive hydration*). In the second case exchange is facilitated (so-called *negative hydration*). Negative hydration is displayed, for example, by the ions K^+, Rb^+ and Cs^+. Thus, according to Samoilov's conception the formation of strong hydration shells does not play the principal part in the process of hydration. While moving, ions possessing negative hydration do not entrain the surrounding water molecules. Ions with positive hydration, for example, Be^{2+} and Mg^{2+}, move together with the first layer, in which translational motion is strongly suppressed.

The Samoilov theory enables one to interpret correctly the diffusion of ions in solutions and to estimate the change of the activity coeficfients of water in the presence of different electrolytes. With

the aid of some additional assumptions Samoilov also determined the coordination numbers of a series of hydrated ions in dilute aqueous solutions. The activation energy U_a characterizes the change in the state of water (or any other solvent) due to the introduction of electrolyte ions, rather than the change in the energy properties of ions. When developed further, Samoilov's theory will probably be able to characterize also the change of the energetic properties of ions in the course of solvation.

3.3. EFFECT OF SOLVATION ON ACTIVITY COEFFICIENTS

In electrolyte solutions ions exist not as free but as solvated particles surrounded by solvent molecules. The departure of the behaviour of electrolytic solutions from ideal systems, and hence the values of activity coefficients reflecting this departure, must therefore depend not only on the ion-ion interaction but on the ion-solvent interaction as well. A theory of electrolytic solutions taking into account both these factors has not yet been developed, but some interesting attempts along this line have already been undertaken. For example, Robinson and Stokes (1949) maintain that all the approximations of the Debye-Hückel theory including the equation

$$\log {}_N f_{\pm} = -\frac{h\sqrt{J}}{1+ab\sqrt{J}} \tag{3.27}$$

yield the activity coefficients not of free but of solvated ions. Empirical activity coefficients refer only to the ionic interaction of unsolvated ions. The connection that exists between the activity coefficients of solvated and unsolvated ions (f' and f, respectively) can be found, taking into account that the chemical potential of a solution does not depend on whether the ions are in the hydrated or in the unhydrated state. Conversely, the chemical potentials of the solvent and the solute will be different in these cases. If n is taken to denote the number of gram-molecules of the solvent used to solvate ν gram-molecules of the solute, then, according to Robinson and Stokes, the following equation will result

$$\log {}_N f'_{\pm} = \log {}_m f_{\pm} + \frac{n}{\nu} \log a_L + \log\left[1 + 0.001 M_L (\nu - n) m\right] \tag{3.28}$$

which interrelates the mean activity coefficients of hydrated ($f'_{\pm}$) and unhydrated ($f_{\pm}$) ions. The mean activity coefficient ${}_N f'_{\pm}$ in expression (3.28) is a rational coefficient, and the mean activity coefficient ${}_m f_{\pm}$ is based on the molality scale; m is the molality of the solute; M_L is the molecular weight of the solvent, and a_L is its activity. Substituting into Eq. (3.28) the value of $\log {}_N f_{\pm}$ from

(3.27) and solving the resulting equation for $\log {}_N f_{\pm}$, we get:

$$\log {}_m f_{\pm} = -\frac{h\sqrt{J}}{1+ab\sqrt{J}} - \frac{n}{\nu}\log a_L - \log\left[1 + 0.001 M_L (\nu - n)\, m\right] \quad (3.29)$$

Equation (3.29) differs from the corresponding equation of the second approximation in the Debye-Hückel theory in that it contains corrections for ion solvation. If the process of solvation is ignored, then the hydration number n will be equal to zero, the second term on the right-hand side of Eq. (3.29) will also vanish, and the third term will reduce to $\log (1 + 0.001\ M_L\, \nu m)$, which corresponds to the coefficient of conversion of the rational activity coefficients ${}_N f$ to the activity coefficients ${}_m f$.

Equation (3.29) includes two empirical constants a and n, the former corresponding in its physical meaning to the shortest possible distance between the hydrated ions and the latter to the hydration number of the electrolyte. Formula (3.28) of the Debye-Hückel ion-finite-size model was derived assuming that the dielectric constants of the solution and solvent are equal; this assumption contradicts reality. In deriving Eq. (3.29) this assumption is preserved, but in this case it is more justified since the greatest change of the dielectric constant is confined to the primary shell of hydration, which is now viewed as an integral part of the solute.

In calculations by Eq. (3.28) experimental hydration numbers can be used; the equation will then contain only one arbitrary constant. The best agreement with experiment is however obtained for other values of n that are not always consistent with n_h values. An explanation of this inconsistency was given by Robinson and Stokes, who found a relation between a and n which reduced the number of arbitrary parameters to a single one. The values of a and n are available in the form of tables compiled by Robinson and Stokes.

Equation (3.29) provides good agreement with experiment up to high concentrations and can therefore be used to compute activity coefficients.

The Robinson-Stokes formula was refined by Izmailov and coworkers (1955-57) who reckoned with the possibility of incomplete dissociation and ionic association and obtained a better fit between theory and experiment (for nonaqueous solutions as well). Using the theory of hydration developed by Samoilov, Solovkin (1961) derived an equation for activity coefficients in which account was taken of ion-solvent interaction. This equation agrees well with data for 1 : 1-valent electrolytes.

3.4. THE PROTOLYTIC THEORY OF ACIDS AND BASES

3.4.1. BRÖNSTED'S THEORY

As is well known, the Arrhenius theory gave rise to dualistic concepts of the nature of acids and bases, according to which the hydrogen ion (proton) is responsible for acidic properties and the hydroxyl ion for basic properties. According to this classical view, acids are substances which dissociate in water to give hydrogen ions, and bases are substances which dissociate to give hydroxyl ions. Hydrogen ions are looked upon as carriers of the catalytic properties of acids, and hydroxyl ions as those of bases. Catalytic activity is considered as one of the most important characteristics of acids and bases. The measurement of the rate of catalytic reactions, say, the reaction of mutarotation of glucose, i.e., transformation of α-glucose into an equilibrium mixture of α- and β-glucose

$$\alpha\text{-glucose} = \alpha\text{-glucose} + \beta\text{-glucose}$$

was even employed to determine the hydrogen ion concentration.

Numerous studies have however demonstrated that not only hydrogen or hydroxyl ions are capable of catalytic action. Unionized acids and bases, acid anions, aniline derivatives and other substances can also function as catalysts. Thus, if catalytic activity is taken to be a characteristic feature of an acid or a base, the definition of these concepts must then be revised. Hydrogen and hydroxyl ions cannot be regarded as the only carriers of acidic and basic properties.

A revision of Arrhenius's concept of acids and bases was also necessitated by the discovery of the phenomenon of ion solvation, especially when the energy effects involved in this process became known. indeed, the chemical energy of hydration of the hydrogen ion is about 260 kcal/g-ion, of which 160 to 180 kcal is evolved when a hydronium ion is formed:

$$H^+ + H_2O = H_3O^+$$

Since

$$-\Delta G = RT \ln K \tag{3.30}$$

where K is the equilibrium constant of the reaction resulting in a hydronium ion:

$$K = \frac{a_{H_3O^+}}{a_{H^+} a_{H_2O}}$$

then, judging by the value of the free energy ΔG, the ratio of the activities of hydronium ions and free hydrogen ions at ordinary temperatures must be of the order of

$$\frac{a_{H_3O^+}}{a_{H^+}} = 10^{140}$$

Thus, there are practically no free hydrogen ions in aqueous solutions, and therefore they cannot be responsible for acidic properties.

A theory of acids and bases that contradicts neither the fact of hydration nor the present-day evidence concerning acid-base catalysis was proposed independently in 1923 by Lowry, Brönsted and Lewis. The most weighty contribution to this theory was made by Brönsted, for which reason it is called *Brönsted's theory.*

According to Brönsted, an acid is defined as a substance that can, in given conditions, donate a proton (a proton-donor) and a base as a substance that can accept a proton (a proton-acceptor):

$$\text{acid} = \text{base} + \text{proton} \qquad (3.31)$$

Brönsted's definition of acids and bases rests upon their attitude to the proton. The theory is therefore also known as the *protolytic theory of acids and bases.*

According to the protolytic theory the ability of a substance to behave either as an acid or as a base depends on the particular conditions of its existence. Under suitable circumstances a substance may act either as a proton-donor, i.e., be an acid, or as a proton-acceptor, i.e., be a base. If a particle loses its proton, that is, exhibits the properties of an acid, the proton must inevitably be accepted by another particle, which will thus play the part of a base. Since this reaction is reversible to some degree or another, the deprotonated particle must possess certain basic properties. It can take the proton back from the particle that has gained it, in which case the latter particle will possess acidic properties. As there are no free protons in solutions, two acid-base pairs must participate in a proton-transfer reaction (acid-base equilibrium):

$$\text{acid}_1 + \text{base}_2 = \text{base}_1 + \text{acid}_2 \qquad (3.32)$$

This general equation of the acid-base equilibrium resembles the equation of the redox reaction:

$$\text{reductant}_1 + \text{oxidant}_2 = \text{oxidant}_1 + \text{reductant}_2$$

where the oxidation-reduction properties are associated with the ability of substances to lose or gain an electron. For example, in the reaction

$$Cu^{+} + Fe^{3+} = Cu^{2+} + Fe^{2+}$$

the electron is transferred from the cuprous ions to the ferric ions. The ions of univalent copper will therefore function as reducing agents, and those of trivalent iron as oxidizing agents. Owing to the reversibility of the reaction, the electrons may move from the ferrous to the cupric ions; in this case the ions of bivalent iron will act as reducing agents and those of bivalent copper as oxidizing agents.

Two acid-base pairs participating in the equilibrium are called *conjugate.* The Brönsted definition of acids and bases and also of conjugate acid-base pairs can be illustrated by the following proton-transfer (or acid-base) reactions:

$$\text{acid}_1 + \text{base}_2 = \text{base}_1 + \text{acid}_2$$
$$HCl + H_2O = Cl^- + H_3O^+$$
$$H_2O + NH_3 = OH^- + NH_4^+$$
$$HCl + NH_3 = Cl^- + NH_4^+$$
$$H_3O^+ + OH^- = H_2O + H_2O$$

According to Brönsted's theory undissociated molecules (e.g , HCl and NH_3), and positive and negative ions (e.g., NH_4^+ and Cl^-) may behave as an acid or as a base.

Thus, "acid" and "base" are relative concepts which are valid under particular conditions. The same substance may behave either as an acid or as a base depending on the nature of the solvent. For instance, water acts as an acid in liquid ammonia and as a base in an aqueous solution of hydrogen chloride. The relative strengths of acids and bases are also dependent on the nature of the solvent. If, say, acetic acid is used as a solvent instead of water (the basic properties of acetic acid being less pronounced compared with water), mineral acids which are completely dissociated in aqueous solutions, will prove weak electrolytes in acetic acid. Their dissociation in acetic acid

$$HA + CH_3COOH = A^- + CH_3COOH_2^+$$
$$\text{acid}_1 + \text{base}_2 = \text{base}_1 + \text{acid}_2$$

will be incomplete, and the dissociation constant will depend on the nature of the acid. In acetic acid as solvent, the strength of mineral acids decreases in the order:

$$HClO_4 > HI > H_2SO_4 > HCl > HNO_3$$

Conversely, in liquid ammonia, which is a stronger base than water, even weak acids, e.g. acetic acid, appear to be practically completely dissociated:

$$CH_3COOH + NH_3 = CH_3COO^- + NH_4^+$$
$$\text{acid}_1 + \text{base}_2 = \text{base}_1 + \text{acid}_2$$

Acetic acid is said to be a differentiating, and ammonia a levelling solvent with respect to acids. Their effect on the dissociation of bases will be reverse. In aprotic solvents, which can neither donate nor accept a proton, say, in benzene, acids and bases will be in the undissociated state. If, however, they are present together, an acid-base interaction may occur between them.

3.4.2. BRÖNSTED'S EQUATION

By making use of the protolytic theory of acids and bases one can arrive at a satisfactory interpretation of the basic regularities of acid-base catalysis. The catalytic effect of an acid is explained by the fact that it is capable of donating its proton to a substance undergoing a chemical change. How readily an acid gives up its proton can be judged by the value of the protolysis constant which is associated with the ionization (or dissociation) constant of the acid. If we denote an acid by A, its conjugate base by B, and the solvent by L, then the protolytic reaction can be written as follows:

$$A + L = B + L' \tag{3.33}$$

where L′ is the deprotonated (acidic) form of the solvent, corresponding to its protonated (basic) form L.

The protolysis constant of the acid A should therefore be represented as

$$K'_A = \frac{c_B c_{L'}}{c_A c_L} \tag{3.34}$$

Assuming that $c_L = \text{const}$, we obtain the ionization constant:

$$K_A = \frac{c_B c_{L'}}{c_A} \tag{3.35}$$

Since the rate of a catalytic reaction depends on how readily an acid donates its proton, i.e., on its strength, then for a series of various acids used as catalysts there must exist a relationship between the acid's dissociation constant K_A and the rate constant k_A of the reaction being catalyzed. This relationship was expressed by Brönsted in the form

$$k_A = \text{const } K_A^{\alpha} \tag{3.36}$$

where α is an arbitrary factor ranging from 0 to 1; Eq. (3.36) is valid also for reactions catalyzed by bases, i.e.,

$$k_B = \text{const } K_B^{\alpha} \tag{3.37}$$

where k_B = rate constant of the reaction catalyzed by bases
K_B = ionization (protonation) constant of conjugate base.

Equations (3.36) and (3.37) are well justified in practice. These equations, known as *Brönsted's equations*, are of much interest. They establish a relation between the thermodynamic (equilibrium constants K_A or K_B) and kinetic (rate constants k_A or k_B) characteristics of a reaction.

On the basis of Brönsted's equations it can be concluded that the change of activation energy in a series of similar reactions must

occur in parallel with the change of the free energy. Indeed, for the reactions concerned

$$-\Delta G = RT \ln K$$

and at the same time the rate constant of the reaction catalyzed is exponentially related to its energy of activation

$$k = \text{const } e^{\frac{-u_a}{RT}}$$

or

$$-u_a = \text{const} + RT \ln k$$

For two acids used to catalyze the same reaction we can write

$$-\Delta G_1 = RT \ln K_{A_1}$$
$$-\Delta G_2 = RT \ln K_{A_2}$$

and

$$-u_{a_1} = \text{const} + RT \ln k_{A_1}$$
$$-u_{a_2} = \text{const} + RT \ln k_{A_2}$$

Taking into account Eq. (3.36), we get

$$\Delta u_a = \alpha\Delta\ (\Delta G) \tag{3.38}$$

that is, the change in activation energy constitutes a certain fraction of the free-energy change.

As an approximation, the free-energy change may be replaced by ΔH:

$$\Delta u_a = \alpha\Delta\ (\Delta H)$$

or by the thermal effect of the reaction at constant pressure:

$$\Delta u_a = -\alpha\Delta\overline{Q}_r$$

From the latter equation it follows that an increase of the thermal effect in a series of similar reactions lowers the energy of activation.

Brönsted's theory is an important step forward as compared with the theories of acids and bases proposed earlier (the ionic theory, the chemical theory of Hantzsch, etc.). But even this theory is not free from shortcomings and does not reflect all the specific features of acid-base interaction.

PART TWO
Nonequilibrium Phenomena In Electrolytic Solutions

An electrolytic solution is at equilibrium if in all its parts sufficiently large as compared with ionic dimensions all the intensive variables are of the same value. The condition for an equilibrium to be attained is the absence of gradients in intensive variables. This condition implies the following:

(1) the temperature of the solution is equal at all points ($T = \text{const}$, $dT/dx = 0$);

(2) the pressure (or the density of the solution) is the same ($P = \text{const}$, $dP/dx = 0$);

(3) there is no potential difference between various parts of the solutions ($\psi = \text{const}$, $d\psi/dx = 0$);

(4) the chemical potential is the same in various parts of the solution ($\mu = \text{const}$, $d\mu/dx = 0$) or, taking into account that μ is a function of activity (concentration), $a = \text{const}$, $da/dx = 0$ or $c = \text{const}$, $dc/dx = 0$.

If even one of these conditions is not observed, processes of thermal diffusion, overflow, electrical conduction or molecular diffusion will occur in the system, as a result of which the corresponding gradient disappears and equilibrium sets in. In the case of electrical conduction the driving force is the electric potential gradient $d\psi/dx$; the driving force for molecular diffusion is the gradient of chemical potential or, roughly speaking, the concentration gradient dc/dx. Since it is ions, i.e., charged particles whose velocities are not equal, that diffuse in electrolytic solutions, diffusion in this case occurs under the combined effect of the concentration and potential gradients. In this respect diffusion is a more complicated process than electrical conduction.

CHAPTER 4

Electrical Conductance of Electrolytic Solutions

4.1. BASIC CONCEPTS

The ionic conduction in an electrolyte is expressed either as the *specific conductance*, or *conductivity* $\varkappa$, or as the *equivalent* (or *molar*) *conductance* λ[1].

The specific conductance, or conductivity, corresponds to the conduction in an electrolyte layer placed between two opposite faces of a cube with 1-cm edges. It is the reciprocal of the *specific resistance* (*resistivity*) ρ:

$$\varkappa = \frac{1}{\rho}$$

The equivalent (or molar) conductance is defined as the conductance of an electrolyte layer of thickness 1 cm placed between two identical electrodes of an area such that the volume of the electrolyte between them contains one gram-equivalent (or 1 g-mole) of solute. The equivalent and specific conductances are interrelated as follows:

$$\lambda = \frac{\varkappa}{c} \text{ or } \lambda = \varkappa V \tag{4.1}$$

where c = concentration of electrolyte, g-eq/ml (or mole/ml)
V = volume of electrolyte, ml, containing, at a given concentration, 1 g-eq (or 1 mole) of solute.

Electrolytes are second-class conductors in which an electric current is transported by ions; the conductance of electrolytes is therefore a function of ionic charge, the velocity of ions, etc.

Suppose that an electrolyte solution of a cross-sectional area equal to Ω is placed between two electrodes (Fig. 4.1). Assume that the distance between two points of the electrolyte in the immediate vicinity of the electrode surfaces is l, and the potential drop on this interval l is equal to $\Delta\psi$. Then, there must exist an electric field gradient ψ' in the electrolytic solution:

$$\psi' = -\frac{d\psi}{dx} = \frac{\Delta\psi}{l} \tag{4.2}$$

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[1] The terms *specific conductivity* and *equivalent* (*molar*) *conductivity* are also occasionally used in the literature (e.g., J.O'M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*). —*Tr.*

If the charge on the ith ion is q_i, this ion will be acted upon by an electric force ${}_e y_i$:

$$ {}_e y_i = - q_i \psi' \tag{4.3} $$

Under the action of this force the ion moves with a certain velocity v_i in a direction parallel to the electric field. Since the ions

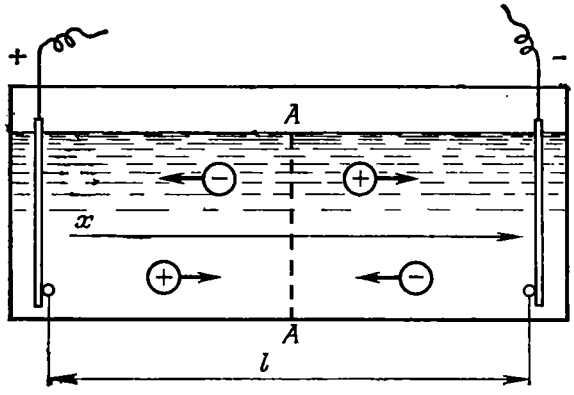

Fig. 4.1. The passage of electric current through electrolyte solutions (schematic)

migrate in a medium of finite viscosity, there must inevitably arise a frictional force ${}_f y_i$ given by

$$ {}_f y_i = k_i v_i \tag{4.4} $$

where ${}_f k_i$ is the frictional coefficient. Under the combined action of these two forces (until they balance) the ion will move with a certain acceleration a_i depending on its mass m_i:

$$ m_i a_i = q_i \psi' - {}_f k_i v_i \tag{4.5} $$

Considering that

$$ a_i = \frac{dv_i}{dt} \quad \text{or} \quad a_i = \frac{d^2x}{dt^2} \tag{4.6} $$

where t is the time, one can obtain, after certain rearrangements, in place of (4.5):

$$ q_i \psi' \, dx = m_i \frac{d^2x}{dt^2} \, dx + {}_f k_i v_i \, dx \tag{4.7} $$

or

$$ q_i \psi' \, dx = d \left(\frac{1}{2} m_i v_i^2 \right) + {}_f k_i v_i \, dx \tag{4.8} $$

Thus, the electric force is used up to impart the ion a certain kinetic energy of movement along the direction of the field, $d\left(\frac{1}{2} m_i v_i^2\right)$, and to overcome the friction force ${}_f k_i v_i \, dx$.

Substituting the value of a_i from (4.6) into (4.5) and integrating, one arrives at the equation of ionic migration in an electric field:

$$v_i = \frac{q_i \psi'}{f k_i} \left(1 - e^{-\frac{f k_i t}{m_i}}\right) \tag{4.9}$$

As the coefficient of internal friction is much greater in absolute value than the mass of the ion ($f k_i \gg m_i$), the quantity $e^{-(f k_i \tau / m_i)}$ will, after a short time τ, become very small as compared with unity and may therefore be neglected. The ion will migrate with a uniform velocity

$$v_i = \frac{q_i \psi'}{f k_i} \tag{4.10}$$

Substitution of the products $z_+ e$ (for positive ions) and $z_- e$ (for negative ions) for q_i in Eq. (4.10) yields expressions for the velocities of cations v_+ and anions v_-

$$v_+ = \frac{z_+ e}{f k_+} \cdot \frac{\Delta\psi}{l} = -\frac{z_+ e}{f k_+} \cdot \frac{d\psi}{dx} \tag{4.11}$$

$$v_- = \frac{z_- e}{f k_-} \cdot \frac{\Delta\psi}{l} = \frac{z_- e}{f k_-} \cdot \frac{d\psi}{dx} \tag{4.12}$$

At $\Delta\psi/l = 1$

$$v_+ = \frac{z_+ e}{f k_+} \equiv v_+^0 \quad \text{and} \quad v_- = \frac{z_- e}{f k_-} \equiv v_-^0 \tag{4.13}$$

where v_+^0 and v_-^0 are the velocities of ionic migration in a given medium at a potential gradient equal to unity. They are termed the *absolute velocities* of ions. It is obvious that

$$v_i = \mp v_i^0 \frac{d\psi}{dx} \tag{4.14}$$

The passage of an electric current through an electrolyte solution (in other words, electrolytic conduction) is made possible by the movement of ions under the influence of an electric field. Since positive and negative ions drift in opposite directions,

$$I = I_+ + I_- \tag{4.15}$$

where I = total current passing through the solution
I_+ and I_- = components of the total current associated with cations and anions, respectively.

If a certain imaginary boundary AA of cross-sectional area Ω is chosen inside an electrolyte (Fig. 4.1), the current intensity will be equal to the number of positive and negative ions crossing this boundary in unit time. All the ions situated at a distance from this boundary corresponding to (or smaller than) their velocity, i.e.,

all the particles contained in a volume $v_i\Omega$, will cross it in one second:

$$I_+ = n_+\Omega v_+^0 \frac{\Delta\psi}{l} z_+ e \tag{4.16}$$

and

$$I_- = n_-\Omega v_-^0 \frac{\Delta\psi}{l} z_- e \tag{4.17}$$

where n_+ and n_- are the number of cations and anions, respectively, per 1 ml of solution. Hence

$$I = I_+ + I_- = \Omega e \frac{\Delta\psi}{l} (n_+ z_+ v_+^0 + n_- z_- v_-^0) \tag{4.18}$$

For a binary electrolyte at infinite dilution it may be assumed that $\alpha = 1$, $z_+ = z_- = z$, and $n_+ = n_- = n$ (n is the number of electrolyte molecules in 1 ml of solution); hence, Eq. (4.18) simplifies to

$$I = I_+ + I_- = nze\Omega (v_+^0 + v_-^0) \frac{\Delta\psi}{l} \tag{4.19}$$

Multiplying and dividing the right-hand side of Eq. (4.19) by Avogadro's number N_A, one has

$$I = I_+ + I_- = czF\Omega (v_+^0 + v_-^0) \frac{\Delta\psi}{l} \tag{4.20}$$

where $c = n/N_A$ is the concentration of the electrolyte in g-eq/ml. Since the ionic velocities v_+^0 and v_-^0 are very low, use is often made in electrochemistry of quantities F times larger. These are called the *ionic mobilities*, or *ionic conductances*:

$$\lambda_+^0 = Fv_+^0 \text{ and } \lambda_-^0 = Fv_-^0 \tag{4.21}$$

Substituting the ionic mobilities λ_+^0 and λ_-^0 for the velocities v_+^0 and v_-^0 in Eq. (4.20) gives

$$I = I_+ + I_- = zc\Omega (\lambda_+^0 + \lambda_-^0) \frac{\Delta\psi}{l} \tag{4.22}$$

or, at $\alpha \neq 1$,

$$I = I_+ + I_- = \alpha zc\Omega (\lambda_+^0 + \lambda_-^0) \frac{\Delta\psi}{l} \tag{4.23}$$

Similarly, for the currents transported by cations and anions,

$$I_+ = \alpha z_+ c\Omega\lambda_+^0 \frac{\Delta\psi}{l} \tag{4.24}$$

and

$$I_- = \alpha z_- c\Omega\lambda_-^0 \frac{\Delta\psi}{l} \tag{4.25}$$

Equations (4.18) and (4.23) express the current intensity in terms of the concentration of an electrolyte, dissociation constant and also the charges and mobilities of those ions into which it dissociates.

Ohm's law

$$\Delta\psi = RI$$

and Eq. (4.23) yield the following expression for the resistance R of a solution:

$$R = \frac{l}{\alpha z c \Omega (\lambda_+^0 + \lambda_-^0)} \tag{4.26}$$

As $R = \rho \frac{l}{\Omega}$, where ρ is the specific resistance, it follows that

$$\rho = \frac{1}{\alpha z c (\lambda_+^0 + \lambda_-^0)} \tag{4.27}$$

Since $\rho = 1/\varkappa$,

$$\varkappa = \alpha z c (\lambda_+^0 + \lambda_-^0) \tag{4.28}$$

and as $\lambda = \varkappa/c$, one has [1]

$$\lambda = \alpha z (\lambda_+^0 + \lambda_-^0) = \alpha \lambda_0 \tag{4.29}$$

where λ_0 is the equivalent (molar) conductance at zero concentration or, which is the same thing, at infinite dilution ($\lambda_0 = \lambda_\infty$).

Comparison of Eqs. (4.23) and (4.29) shows that the equivalent conductance corresponds to the quantity of electricity transported by 1 g-eq of ions per second (i.e., to current intensity) through a cross-sectional area of 1 cm^2 at a potential gradient of 1 V/cm.

In some cases one has to know the fraction of the total current carried by a particular ionic species, or what is known as the *transport numbers* (or the *transference numbers*) of positive and negative ions.

In the equations

$$t_+ = \frac{I_+}{I} \tag{4.30}$$

and

$$t_- = \frac{I_-}{I} \tag{4.31}$$

t_+ and t_- are the transport numbers of positive and negative ions, respectively. Substituting the values of I, I_+ and I_- from Eqs. (4.23), (4.24) and (4.25) into Eqs. (4.30) and (4.31), we obtain expressions for the transport numbers of a binary electrolyte in terms of ionic mobilities:

$$t_+ = \frac{\lambda_+^0}{\lambda_+^0 + \lambda_-^0} \tag{4.32}$$

and

$$t_- = \frac{\lambda_-^0}{\lambda_+^0 + \lambda_-^0} \tag{4.33}$$

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[1] The experimental value of conductivity $\varkappa$ includes the conductance of the solvent, and so when the equivalent conductance λ is calculated, use should be made of the quantity $\varkappa$ corrected for this effect.

Here

$$t_+ + t_- = 1 \tag{4.34}$$

For any electrolyte as well as for solutions containing several electrolytes, the transport number of an ionic species i is expressed by the equation

$$t_i = \frac{I_i}{\Sigma I_i} \tag{4.35}$$

In this case

$$\Sigma t_i = 1 \tag{4.36}$$

where the summation is carried out over all the ionic species.

4.2. PRINCIPLES OF EXPERIMENTAL DETERMINATION OF CONDUCTANCE

4.2.1. MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES

The conductance of electrolytes is usually determined by means of a bridge circuit used for measuring the resistance of first-class conductors (metals). In the case of electrolytic solutions use is made of alternating-current bridge circuits because the passage of a direct current through solutions leads to considerable errors due to electrolysis and polarization. The necessity of using an alternating current of sufficiently high frequency (in order to avoid the errors mentioned) complicates the measuring circuit. Apart from a bridge, the circuit includes an a-c generator and special apparatus used to rectify the current before it passes through the null indicator and to compensate for the capacity effects. Present-day apparatus for measuring the conductance of electrolytes, in which all the specific features of second-class conductors are taken into account, yields reliable results.

4.2.2. METHODS FOR DETERMINATION OF TRANSPORT NUMBERS AND IONIC MOBILITIES

Hittorf's Method. A number of methods for the determination of transport numbers have been suggested. The first method was developed by Hittorf and later refined by Findlay, Kistyakovsky, and others.

Hittorf's method is based on the general equation of transport numbers:

$$t_i = \frac{I_i}{\Sigma I_i} = \frac{I_i}{I} \tag{4.37}$$

It makes use of the fact that the concentration of an electrolyte near the electrodes (in the anodic and cathodic regions) changes as a re-

sult of the passage of a direct current through the electrochemical system and of the associated directional movement (drift) of ions. The amount of displaced gram-equivalents of a given ionic species is related with the fraction of current borne by each ion and may be represented in the form of the expression $(I_i/F)\tau$, where τ is the time during which the current passed through the system. The total number of transported gram-equivalents (faradays) of electricity is written in a similar way:

$$\frac{I}{F}\tau$$

The equation for the transport number of a particular ionic species will thus have the form:

$$t_i = \frac{\frac{I_i}{F}\tau}{\frac{I}{F}\tau} = \frac{\text{number of transported gram-equivalents of substance}}{\text{number of faradays passed through the system}} \qquad (4.38)$$

The number of transported gram-equivalents of a substance can be found analytically from the concentration changes in the anolyte and catholyte. The total quantity of electricity passed is determined with a coulometer (see page 305).

Suppose we have an electrochemical system

$$\text{Hg, K/KCl/K, Hg} \quad (\rightarrow)$$

through which a current is passed in the direction indicated by the arrow. The left electrode is the anode, and the right the cathode. Potassium dissolves at the anode and its ions pass into solution. The potassium ions move toward the cathode where they are discharged to form an amalgam. The chloride ions migrate from the cathode to the anode, i.e., in a direction opposite to the movement of the potassium ions. The migration of both ionic species occurs according to their transport numbers. The scheme of the processes taking place in the system when one faraday of electricity is passed through it may be represented as follows:

	Anodic region	Cathodic region
Electrode reaction	$K \rightarrow K^+$	$K^+ \rightarrow K$
Migration	$-t_+K^+ + t_-Cl^-$	$+t_+K^+ - t_-Cl^-$
Total . . .	$-K + (1 - t_+)\,K^+ + t_-Cl^-$	$+K - (1 - t_+)\,K^+ - t_-Cl^-$
or	$-K + t_-K^+ + t_-Cl^-$	$+K - t_-K^+ - t_-Cl^-$

since the solution contains only a binary 1 : 1-valent electrolyte, for which, according to Eq. (4.34),

$$1 - t_+ = t_-$$

From the scheme given above, the so-called *electrode-balance scheme*, it follows that the passage of one faraday through the system results in the migration of one gram-atom of potassium from the anode to the cathode and that the amount of potassium chloride will increase by t_- g-eq at the anode and decrease by the same amount at the cathode. Let the initial concentration of KCl be c_0 and the volumes of the anolyte and catholyte V_a and V_k, respectively; then the concentrations c_a and c_k in the anodic and cathodic regions [1] after the passage of one faraday will be, respectively,

$$c_a = c_0 + \frac{t_-}{V_a} \quad \text{and} \quad c_k = c_0 - \frac{t_-}{V_k} \tag{4.39}$$

from which

$$t_- = \Delta c_a V_a \quad \text{and} \quad t_- = -\Delta c_k V_k$$

If the number of faradays is z, then

$$t_- = \frac{\Delta c_a V_a}{z} \quad \text{and} \quad t_- = -\frac{\Delta c_k V_k}{z} \tag{4.40}$$

Hence, in accord with Eq. (4.38), to determine the transport numbers of ions by Hittorf's method it is necessary to know the total quantity of electricity passed and the number of gram-equivalents of the substance transported.

If, instead of a soluble amalgam anode, use is made of an insoluble platinum anode

$$\text{Pt/KCl/K, Hg} \quad (\rightarrow)$$

chlorine will be deposited at the anode and the electrode-balance scheme will assume the form:

	Anodic region	Cathodic region
Electrode reaction	$Cl^- \rightarrow \frac{1}{2} Cl_2$	$K^+ \rightarrow K$
Migration	$-t_+K^+ + t_-Cl^-$	$+t_+K^+ - t_-Cl^-$
Total	$-t_+KCl + \frac{1}{2} Cl_2$	$-t_-KCl + K$

Here the concentration of the substance decreases both in the anodic and the cathodic region. Using the previous notation, one can now write

$$t_+ = -\frac{\Delta c_a V_a}{z} \tag{4.41}$$

and

$$t_- = -\frac{\Delta c_k V_k}{z} \tag{4.42}$$

Since

$$t_+ + t_- = 1$$

[1] It is assumed that the volumes of the anolyte and catholyte are larger than the thickness of the solution layer in which diffusion takes place.

from Eqs. (4.41) and (4.42) it follows that

$$-\left(\frac{\Delta c_a V_a}{z}+\frac{\Delta c_k V_k}{z}\right)=1$$

or

$$z=-(\Delta c_a V_a+\Delta c_k V_k)$$

The transport numbers in this system can be found without a coulometer by using experimental data on the change of the electrolyte concentration in the anodic and cathodic regions:

$$t_+=\frac{\Delta c_a V_a}{\Delta c_a V_a+\Delta c_k V_k} \tag{4.43}$$

and

$$t_-=\frac{\Delta c_k V_k}{\Delta c_a V_a+\Delta c_k V_k} \tag{4.44}$$

By choosing suitable electrochemical systems one can determine transport numbers for any electrolyte.

The Moving Boundary Method. The second method of determining transport numbers which has recently found wide application is known as the *moving boundary method.* The essence of this method is as follows: a given amount of current is passed and after a definite time the distance travelled by the boundary between two solutions with a common ion is determined. The boundary between two solutions is particularly sharply defined if one of them is coloured. If both solutions are colourless but have different densities, the boundary will be visible because of the difference in their refractive indices. In either case the movement of the boundary is easily followed with the aid of a reading microscope.

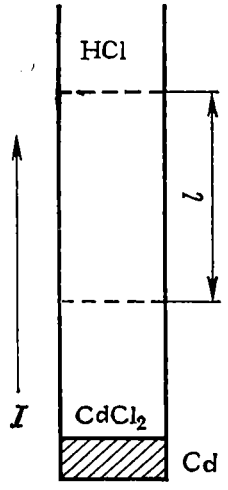

Fig. 4.2. Measurement of ionic mobilities (transport numbers) by the moving boundary method

Figure 4.2 shows the principle of determining the mobility of cadmium ions by the moving boundary method. When a current is passed through the solution in the direction indicated in Fig. 4.2, cadmium ions appear in it and a boundary is formed between the solutions of cadmium chloride and hydrochloric acid. As the current flows the boundary moves upwards. If the boundary travels, in a time τ, a distance l equivalent to the volume $V = l\Omega$, where Ω is the cross section of the tube, the number of gram-equivalents of $CdCl_2$ transferred will be equal to cV, where c is the concentration of $CdCl_2$. With a current intensity I the total quantity

of electricity passed will be equal to $I\tau/F$ faradays and hence the transport number of the Cd^{2+} ion will be [1]

$$t_+ = \frac{cVF}{I\tau} \tag{4.45}$$

which corresponds to Eq. (4.38).

The boundary between the $CdCl_2$ and HCl solutions is sharply defined because of the different conductivities of the electrolytes. In the case under consideration $\varkappa_{HCl} > \varkappa_{CdCl_2}$ and $IR_{(HCl)} < IR_{(CdCl_2)}$ or $(\Delta\psi/l)_{HCl} < (\Delta\psi/l)_{CdCl_2}$, i.e., the potential gradient is higher in the $CdCl_2$ than in the HCl solution. Therefore, if, as a result of a temporary interruption of current, the faster hydrogen ions appear in the zone of $CdCl_2$, then under the influence of the increased potential gradient they will outrun the slower Cd^{2+} ions and return into the region of hydrochloric acid. Conversely, if the Cd^{2+} ions move into the hydrochloric acid zone, their velocity will fall owing to the decreased potential gradient. They will lag behind the H^+ ions and appear again in the solution of cadmium chloride. For the boundary to be sharply defined the optimal concentrations of indicator solutions are usually chosen in preliminary experiments such that will ensure the observance of the so-called Kohlrausch regulating ratio:

$$\frac{t_L}{t_F} = \frac{c_L}{c_F}$$

where the subscripts F and L refer, respectively, to electrolytes with fast and slow ions (in our case, to the solutions of HCl and $CdCl_2$).

The data obtained by the two methods described above are in agreement. [2]

Determination of Ionic Mobilities. Experimental data on electrical conductance and transport numbers can be used to calculate ionic mobilities. From Eq. (4.29) it follows that for a 1 : 1-valent electrolyte at infinite dilution, where the degree of dissociation α is equal to unity, the equivalent conductance is the sum of ionic mobilities:

$$\lambda_\infty = \lambda_+^0 + \lambda_-^0 \tag{4.46}$$

In place of Eqs. (4.32) and (4.33) one may write:

$$t_+^0 = \frac{\lambda_+^0}{\lambda_\infty} \quad \text{and} \quad t_-^0 = \frac{\lambda_-^0}{\lambda_\infty} \tag{4.47}$$

from which one can easily find ionic mobilities at infinite dilution using the known t_+^0 and λ_∞ values.

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[1] If the concentration of HCl is inserted into Eq. (4.45), in place of $CdCl_2$, it will yield the transport number of hydrogen ions in hydrochloric acid.

[2] The third method for determining transport numbers is based on emf measurements and will be discussed later (see Sec. 9.1).

An equation analogous to Eq. (4.47) is valid not only at infinite dilution but also at any concentration c in the case of binary electrolytes. This can be easily illustrated by substituting the values of the corresponding currents from (4.23), (4.24) and (4.25) into Eqs. (4.30) and (4.31); this substitution gives:

$$t_+ = \frac{\lambda_+}{\lambda_\infty} \quad \text{and} \quad t_- = \frac{\lambda_-}{\lambda_\infty} \tag{4.48}$$

where λ_i is the ionic mobility in a solution of concentration c.

4.3. EXPERIMENTAL DATA ON THE CONDUCTANCE OF ELECTROLYTE SOLUTIONS

4.3.1. RELATION BETWEEN CONDUCTANCE AND THE PROPERTIES OF ELECTROLYTES AND THE NATURE OF SOLVENT

The electrical conductance of electrolyte solutions depends first of all on the nature of the electrolyte and solvent. If we compare the values of equivalent conductance as measured in aqueous solutions at infinitely large dilution, acids will be found to have the highest values, followed by bases and salts in decreasing order (see Table 4.1).

TABLE 4.1

Equivalent Conductances of Some Electrolytes in Infinitely Dilute Aqueous Solutions at 25°C

Electrolyte	λ_∞	Electrolyte	λ_∞	Electrolyte	λ_∞
H_2SO_4	429.8	KOH	271.1	KCl	149.9
HCl	426.2	NH_4OH	271.0	KNO_3	145.0
HNO_3	421.2	NaOH	247.8	NaCl	126.4

The effect of the nature of an electrolyte or, more precisely, the nature of its constituent ions will become even more prominent if we consider a series of ionic mobilities also corresponding to infinite dilution (see Table 4.2).

As can be seen from Table 4.2, in a series of ions of equal valency the electrolytic mobility increases with increasing ionic radius r_i (an exception is the higher mobility of bromide ions as compared with iodide ions). With equal or similar radii the mobilities of cations are greater than those of anions. While the mobilities of all ions differ little from each other, the hydroxyl ions, and especially the hydrogen ions, possess abnormally high mobilities, 3 to 8 times greater than those of the other ions.

TABLE 4.2
Electrolytic Ionic Mobilities in Aqueous Solutions at Infinite Dilution at 25°C

Ion	Ag^+	$\frac{1}{3}Al^{3+}$	$\frac{1}{2}Ba^{2+}$	Br^-	$\frac{1}{2}Ca^{2+}$	$\frac{1}{2}Cd^{2+}$	Cl^-	ClO_4^-	Cs^+	$\frac{1}{2}Cu^{2+}$
r_i, Å	1.13	0.57	1.38	1.96	1.04	0.99	1.81	—	1.65	0.80
λ_i^0	61.9	63.0	63.7	78.3	59.5	54.0	76.3	68.0	76.8	54.0
Ion	F^-	$\frac{1}{2}Fe^{2+}$	$\frac{1}{3}Fe^{3+}$	H^+	$H_2PO_4^-$	$\frac{1}{2}HPO_4^{2-}$	I^-	K^+	$\frac{1}{3}La^{3+}$	Li^+
r_i, Å	1.23	0.80	0.67	—	—	—	2.20	1.33	1.04	0.68
λ_i^0	55.4	53.5	68.0	349.8	36.0	57.0	76.8	73.5	69.5	38.7
Ion	$\frac{1}{2}Mn^{2+}$	Na^+	$\frac{1}{2}Ni^{2+}$	NH_4^+	NO_3^-	OH^-	$\frac{1}{2}Pb^{2+}$	Rb^+	$\frac{1}{2}SO_4^{2-}$	$\frac{1}{2}Zn^{2+}$
r_i, Å	0.74	0.98	0.74	—	—	—	1.26	1.49	—	0.83
λ_i^0	53.1	50.1	54.0	73.7	71.4	197.6	70.0	77.5	80.0	53.5

The values of transport numbers as derivatives of ionic mobilities depend on the nature of the electrolyte. The hydrogen ion has the largest transport number among the cations, and the hydroxyl ion among the anions.

When solvents other than water are used, changes are observed in electrical conductance, ionic mobility and, to a lesser degree, in transport numbers. The main properties of a solvent that determine the character of variation of electrical conductance are its viscosity and dielectric constant. An increase in viscosity leads to a decrease in conductance. This effect was formulated quantitatively by Pisarzhevsky and Walden and is known as the *Pisarzhevsky-Walden rule*:

$$\lambda_0 \gamma_0 = \text{const} \tag{4.49}$$

where λ_0 = equivalent conductance of electrolyte extrapolated to zero concentration

γ_0 = viscosity of pure solvent.

A similar relation also exists for ionic mobilities:

$$\lambda_i^0 \gamma_0 = \text{const} \tag{4.50}$$

The effect of the dielectric constant of a solvent reveals itself especially noticeably in the character of variation of electrical conductance with concentration, giving rise to so-called abnormal conductance curves.

4.3.2. EFFECT OF CONCENTRATION, TEMPERATURE AND PRESSURE ON THE CONDUCTANCE OF ELECTROLYTE SOLUTIONS

In aqueous (and most nonaqueous) solutions, with increasing concentration of the solution, the specific conductance of the electrolytes first increases, reaching a certain maximum, and then falls with further increase of concentration. The position of the maximum depends on the nature of the electrolyte and its temperature. The concentration dependence of conductivity for a series of electrolytes is shown in Fig. 4.3.

The equivalent conductance of aqueous solutions of electrolytes diminishes with increasing concentration (Fig. 4.4). The highest equivalent conductance is observed at zero concentration, when $\lambda_c = \lambda_0$. The equivalent conductance λ is often expressed as a function of dilution V. In this case, as would be expected, the equivalent conductance is found to increase with dilution, and at high dilutions it approaches a certain limiting value. This limiting value is called the *equivalent conductance at infinite dilution*, denoted by the symbol λ_∞ (Fig. 4.5). For a given electrolyte the equivalent conductance at zero concentration is naturally the same as the equivalent conductance at infinite dilution.

Kohlrausch found that in the region of low concentrations the equivalent conductance of a strong electrolyte varies with concentration according to the empirical equation

$$\lambda_c = \lambda_0 - A\sqrt{c} \tag{4.51}$$

known as the *square root law* (A is an empirical constant).

At somewhat higher concentrations of strong electrolytes a better agreement with experiment is furnished by the equation

$$\lambda_c = \lambda_0 - A\sqrt[3]{c} \tag{4.52}$$

which is known as the *cubic root law*. For dilute solutions of weak electrolytes the following equation holds true:

$$\log \lambda_c = \text{const} - \frac{1}{2}\log c \tag{4.53}$$

When one switches from water to nonaqueous solvents possessing a high dielectric constant, no noticeable changes in the character of the concentration dependence of electrical conductance are observed. However, in solutions with a low dielectric constant (for example, in a mixture of water and dioxan) the course of the equivalent conductance-concentration curve typical of aqueous solutions is disturbed

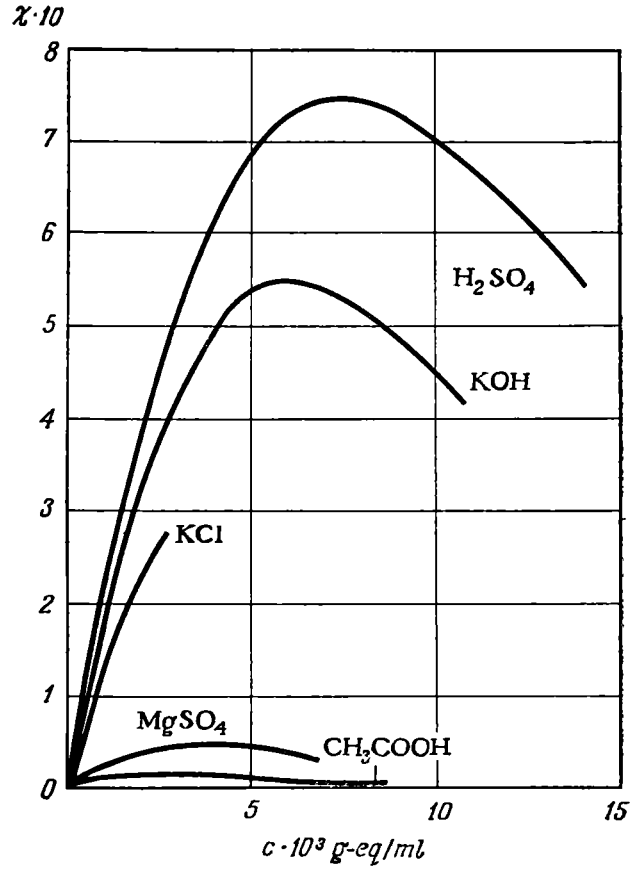

Fig. 4.3. The variation of specific conductance (conductivity) with concentration for some electrolytes

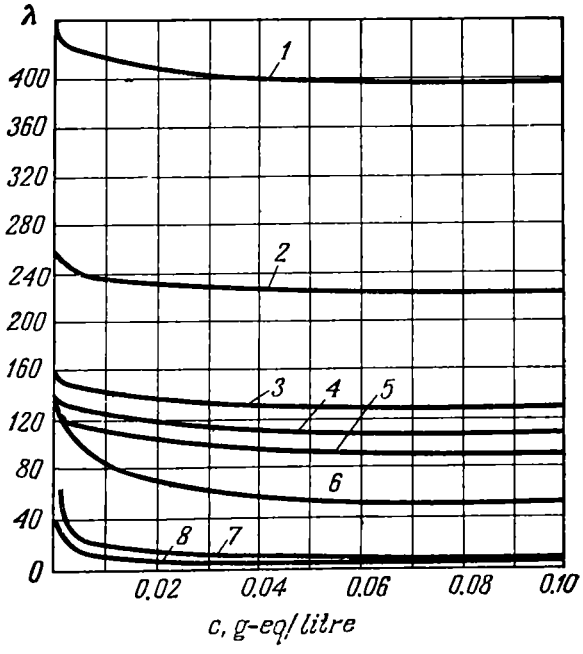

Fig. 4.4. The variation of equivalent conductance with concentration for some electrolytes:

1—hydrochloric acid; *2*—sodium hydroxide; *3*—potassium chloride; *4*—silver nitrate; *5*—sodium sulphate; *6*—copper sulphate; *7*—acetic acid; *8*—ammonium hydroxide

and extrema appear on it. Figure 4.6 shows the concentration dependence of the equivalent conductance typical of such solutions

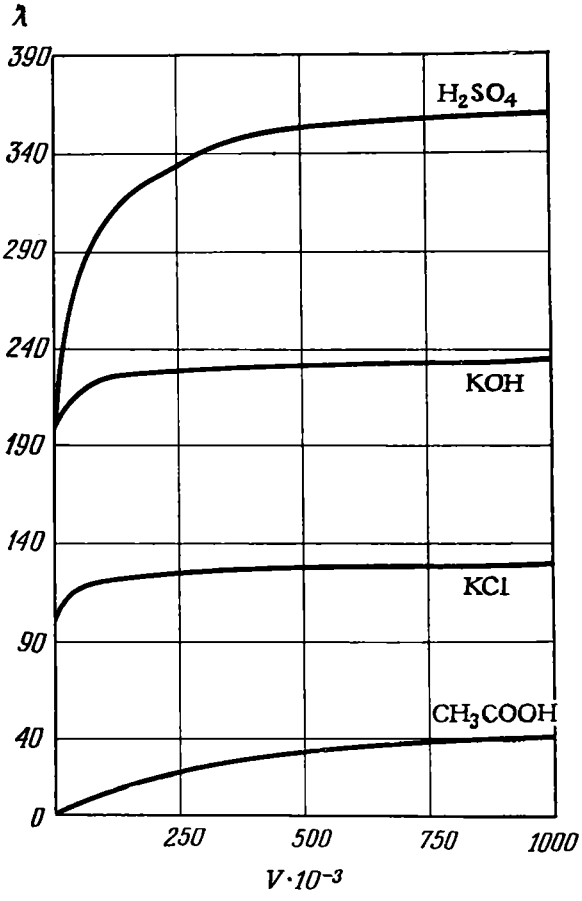

Fig. 4.5. Dependence of equivalent conductance on dilution in aqueous solutions of some electrolytes

The temperature dependence of the equivalent conductance for a narrow range of temperatures may be represented by the equation

$$\lambda_t = \lambda_{t=0}(1 + \alpha t) \tag{4.54}$$

or for a wider range of temperatures

$$\lambda_t = \lambda_{t=0}(1 + \alpha t - \beta t^2) \tag{4.55}$$

where λ_t and $\lambda_{t=0}$ = equivalent conductances at temperatures t and 0° C, respectively

α and β = empirical coefficients.

The dependence of the specific conductance of dilute solutions on temperature is described by Kohlrausch's formula, which is similar to Eq. (4.55),

$$\varkappa_t = \varkappa_{t=25}\,[1 + \alpha'(t - 25) + \beta'(t - 25)^2] \tag{4.56}$$

with the only difference that the standard temperature is taken to be 25°C.

The coefficient α' depends on the nature of the electrolyte; it equals 0.0164 for strong acids, 0.0190 for strong bases and 0.0220 for salts. In the case of weak electrolytes the coefficients α' are higher than for strong electrolytes. The coefficient β' increases regularly with increasing α'; the relation between the two coefficients is expressed by the following empirical equation:

$$\beta' = 0.0163\ (\alpha' - 0.0174) \quad (4.57)$$

It should be noted that the temperature coefficients of the conductance of aqueous solutions and those of the viscosity of water are close in magnitude but opposite in sign.

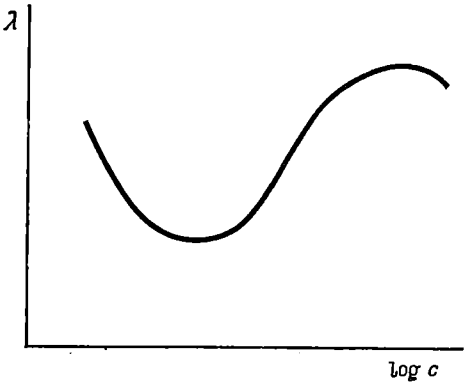

Fig. 4.6. Anomalous conductance curve for an electrolyte in a non-aqueous solvent

Transport numbers vary with concentration to a lesser degree than the conductance of electrolytes. The variation of transport numbers with concentration is less pronounced than in the case of the conductance of electrolytes. Some experimental data characterizing the concentration dependence of transport numbers are presented in Table 4.3. [1] It follows from this table that if the transport number

TABLE 4.3

Dependence of the Transport Numbers of Cations on Concentration at 18°C

Electrolyte	Transport number of cations at an electrolyte concentration of, g-eq/litre							
	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1
LiCl	—	0.332	0.328	0.320	0.313	0.304	—	—
NaCl	0.396	0.396	0.396	0.395	0.393	0.390	0.382	0.369
KCl	0.496	0.496	0.496	0.496	0.495	0.494	—	—
HCl	0.832	0.833	0.833	0.834	0.835	0.837	0.840	0.844
$AgNO_3$	—	0.471	0.471	0.471	0.471	—	—	—
$CdSO_4$	—	0.389	0.384	0.375	0.365	0.350	0.323	0.294

is larger than 0.5, it is found to increase further with increasing concentration. Conversely, if $t_i < 0.5$, it decreases still further as the

[1] In a series of such compounds, at any concentration, the transport number of a cation increases with its radius.

concentration increases. In concentrated solutions transport numbers may assume negative values, this being attributed to the formation of complex ions. For example, for silver cyanide in an excess of potassium cyanide the transport number of the Ag^+ ions will be negative. Here silver enters into the composition of a complex anion and migrates to the anode when a current is passed.

A stronger effect on transport numbers (provided they are different from 0.5) is exerted by temperature. Table 4.4 gives some experimental data for several electrolytes in 0.02*N* solutions. It is seen

TABLE 4.4

Temperature Dependence of Transport Numbers of Cations

Electrolyte	Transport numbers of cations at			
	0°C	18°C	30°C	96°C
NaCl	0.387	0.396	0.404	0.442
$AgNO_3$	0.461	0.471	0.481	—
HCl	0.844	0.833	0.822	0.748

from Table 4.4 that with increasing temperature the transport numbers are equalized, i.e., if they exceeded 0.5 they become lower and, conversely, transport numbers smaller than 0.5 increase.

The mobility of ions is dependent on the concentration and temperature of the electrolyte (see Tables 4.5 and 4.6), the nature of this dependence being analogous to that observed for the electrical

TABLE 4.5

Concentration Dependence of Absolute Ionic Mobilities ($v_i^0 \cdot 10^5 cm^2 \cdot sec^{-1} \cdot V^{-1}$) at 18°C

Ion	Absolute ionic mobility at a concentration of, g-eq/litre						
	1×10⁻⁴	2×10⁻⁴	5×10⁻⁴	1×10⁻³	2×10⁻³	8×10⁻³	1×10⁻²
Na^+	—	47.3	—	—	44.2	—	41.5
K^+	—	—	67.0	65.0	—	—	—
Zn^{2+}	—	—	46.5	47.2	45.5	41.0	—
Cl^-	68.0	67.5	66.5	—	—	—	—
SO_4^{2-}	73.0	71.5	69.5	69.5	—	—	—
NO_3^-	—	—	—	—	—	58.5	57.5

conductance of electrolytes. A rise of temperature increases the mobility of all ions, and the higher the ionic conductance, the lower the temperature coefficient of the ionic mobility.

TABLE 4.6

Temperature Dependence of the Mobility of Some Ions

Ion	Limiting ionic mobility at		
	0°C	18°C	100°C
Li^+	17.8	33.5	120
Na^+	25.5	43.5	150
K^+	40.3	64.5	200
Cl^-	41.2	65.5	207
Br^-	—	67.7	—
H^+	—	315.0	637
OH^-	—	175.4	446

Apart from temperature, the conductance of weak and strong electrolytes is also affected by the pressure experienced by the solution. It has been found, for example, that at low temperatures (up to 20°C) the conductance of acetic acid solutions falls with increasing pressure. At higher temperatures the same solutions show a certain rise in conductance as the pressure increases. The equivalent conductance of the majority of strong electrolytes has been found to increase as the pressure increases from atmospheric to 50-100 kg/cm^2 (depending on the nature of the electrolyte). A further increase in pressure lowers the conductance, bringing it below those corresponding to the atmospheric pressure. Experiment shows that the variation of the conductance of strong electrolytes with pressure obeys the same law that governs fluidity (which is the reciprocal of the viscosity of a liquid).

4.4. CONDUCTOMETRY

4.4.1. CLASSICAL CONDUCTOMETRY

The value of the electrical conductance of solutions plays a major part in electrochemical processes. It may be used as a basis for rational selection of the composition of an electrolyte, thereby reducing the unproductive consumption of electrical energy to a minimum. A knowledge of the conductance of solutions is needed in drawing up energy and heat balances for electrolytic cells and chemical sources of electricity. The throwing power of galvanic baths (the ability of producing a uniform metal layer on areas situated at different distances from the anode) strongly depends on the value of conductance. Data on conductance measurements are used not only in electrochemistry. Conductometry finds wide application as a method of chemical analysis, production control and scientific research. Conductometry has a number of advantages over chemical methods of analysis since it enables determination of the content of an individual substance in a solution by simply measuring the conductance of the solution. To do this, it is sufficient to have a conductance-concentra-

tion calibration curve. Besides, the solution being analysed undergoes practically no change in the course of conductance measurements, which makes it possible to measure its conductance several times and keep the solution in order to check the results at any time.

Conductometric analysis is one of the most precise techniques for determining the solubilities of sparingly soluble substances. It is based on the measurement of the conductance of a liquid phase in equilibrium with the corresponding solid substance. Knowing the mobilities of the ions into which a particular sparingly soluble substance dissociates and the conductivity of the solution, one can calculate its concentration by using the equation

$$c = \frac{\varkappa}{z\alpha f_\lambda (\lambda_+^0 + \lambda_-^0)} \tag{4.58}$$

Since a salt is sparingly soluble, i.e., its concentration in solution is very small, the degree of dissociation α and the conductance coefficient f_λ (see below) may be assumed to be equal to unity, and the ionic mobilities in a given solution λ_+ and λ_- equal to those at infinite dilution λ_+^0 and λ_-^0. If the concentration c is known, it is easy to find the solubility of the substance. Conductometry is also employed to determine the equilibrium constants of chemical reactions in solutions, the basicity of acids, etc.

In contrast to ordinary titration techniques, conductometric titration does not require the use of indicator solutions and can be carried out in coloured as well as in very dilute solutions. During titration the course of the reaction is followed and the conductance of the solution being titrated is measured after each addition of the titrating reagent. The end point of titration coincides with the inflection on the curve of conductance against the volume of solution added. The change in conductance during conductometric titration is associated with the replacement of some ions by others with a different ionic conductance.

Suppose we have an alkaline solution which is to be titrated with an acid. Suppose the solution taken for titration contains a g-eq of NaOH. Its conductance is determined by the mobilities of the ions Na^+ and OH^-, which are equal, at 25°C, to 50.1 and 197.6, respectively. To this solution is added an amount of titrating solution containing x g-eq of HCl. If $x < a$, partial neutralization of the alkali by the acid will occur:

$$a\,(Na^+ + OH^-) + x\,(H^+ + Cl^-) = x\,(Na^+ + Cl^-) + \\ + xH_2O + (a - x)\,(Na^+ + OH^-)$$

As a result of incomplete neutralization, $(a - x)$ g-eq of NaOH will remain in the solution being titrated and x g-eq of NaCl will appear as Na^+ and Cl^- ions of mobilities 50.1 and 76.3, respectively. Thus, some of the hydroxyl ions are replaced by less mobile chloride ions and the conductance of the solution diminishes. This will take place

after the addition of each new portion of hydrochloric acid solution until the equivalence point is reached, at which all the OH^- ions of the alkali will be replaced by Cl^- ions. Upon further addition of the titrating solution (beyond the point of equivalence) the acid will no longer associate with the alkali. The alkali will be completely neutralized and free hydrogen ions possessing a very high mobility (equal to 349.8) will appear in the titrate along with chloride ions. This will lead to a sharp increase of conductance (Fig. 4.7). The minimum on the conductance curve is the equivalence point which corresponds to the conductance of sodium chloride. The content of the base in the titrate can easily be calculated from the volume of acid used up until the minimum point is reached.

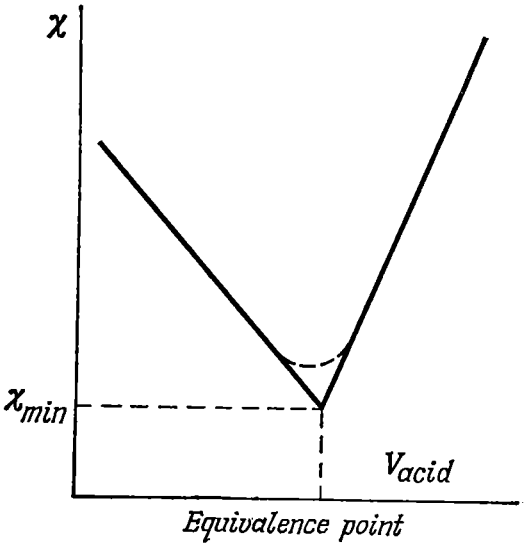

Fig. 4.7. Graph of conductometric titration of an alkaline solution by an acidic solution

The example just quoted shows that the sensitivity of conductometric titration depends very strongly on the difference in the mobilities of the associated and appearing ions, and the greater this difference the higher is the sensitivity. In carrying out conductometric titrations one should take into account not only the degree of completeness of the principal reaction; of great importance are also the mobilities of ions that do not participate directly in the reaction.

Another feature distinguishing the conductometric titration from the ordinary procedure is that it yields not just a single point (the point of neutralization associated with the change of the colour of the solution in the case of volumetric titration with an indicator and coinciding with the minimum on the $\varkappa$ vs. V curve) but also the full curve for the entire process of titration. On the basis of this curve one can get an idea not only of the course of the reaction but also of some properties of the substances obtained. For example, a sharp minimum or a distinct inflection on the conductance curve is evidence of the stability or low solubility of the reaction products. A blurred region of transition from one portion of the curve to another points either to hydrolysis of the salt formed or to a high solubility of the precipitate, or else to an insufficient stability of the new substance (depending on the nature of the principal reaction). If certain conditions are observed, it is possible to determine conductometrically two different substances present in the same solution.

An interesting feature of the conductometric method of production control is that changes in the system under test take the form of electrical signals. Electrical pulses can be transmitted directly to the actuating mechanism, which facilitates the automatic control of the process. The electrical conductance of a solution depends on all the components present and is therefore an integral property of the system. A combination of conductance measurement with determination of any other integral (e. g., density) or specific (e.g., the pH value) property of a solution allows the system of automatic control to be improved. Conductometry is successfully utilized for the control of precipitate washout, regeneration of ion-exchange resins, water purification and of many other technological processes.

The conductometric method cannot however be employed for the determination of a single ionic species against the background of other electrolytes. This is because the latter possess their own conductance and will mask the change of conductance corresponding to the change in the concentration of the ionic species to be determined in the course of conductometric titration, which will naturally reduce the accuracy of the method and limit the range of its applicability.

4.4.2. HIGH-FREQUENCY CONDUCTOMETRY

So-called *high-frequency conductometry* (*high-frequency titration*) has been gaining an ever increasing application. In this method use is made of alternating currents of frequencies of the order of several millions of hertz. With these frequencies the electrodes may be removed from the solution and placed outside the cell (in which measurements are made). This eliminates many difficulties involved in ordinary conductometry, namely, the catalytic effect of electrodes on the reactions taking place in solutions, the change of electrode surfaces during the measurements, the necessity of using electrodes made of noble metals (metals resistant to the action of a solution), etc.

In high-frequency titrations [1] a measuring cell made of glass or plastic and containing the solution to be tested is placed either between two metallic plates tightly secured against the outer walls of the cell (a cell of the capacitive type) or inside a self-induction coil (a cell of the inductive type). In high-frequency conductometry it is not the conductance of the solution that is measured, but a set of many properties of the solution and cell, including the dielectric constant. The interpretation of the results obtained by this method is therefore more complicated than in the case of conventional conductometry.

The high-frequency technique is successfully employed for analytical purposes and in scientific investigations.

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[1] Such titrations were recently renamed *oscillometric titrations.—Tr.*

CHAPTER 5

Theoretical Interpretation of the Electrical Conductance of Electrolytes

5.1. CLASSICAL THEORY

The relation between specific conductance and concentration is expressed by a curve with a maximum (see Fig. 4.3). To account for the appearance of a maximum the classical theory makes use of the equation

$$\varkappa = \alpha c (\lambda_+^0 + \lambda_-^0)$$

It is presumed here that the term enclosed in parentheses is independent of the concentration, and the degree of electrolytic dissociation diminishes with increasing concentration. Therefore, at a definite concentration the product αc and hence $\varkappa$ will have the highest value.

Usanovich has shown that this explanation in fact does not agree with the basic principles of the classical theory of electrolytic solutions. It is known that the degree of dissociation of an electrolyte α and its concentration c are interrelated by the equation

$$K = \frac{\alpha^2 c}{1-\alpha}$$

whence

$$\alpha c = K \frac{1-\alpha}{\alpha}$$

From the last equation it follows that with rising concentration the product αc must also increase regularly because the ratio $(1 - \alpha)/\alpha$ will grow continuously. For this reason one cannot expect the appearance of an extremum on the conductivity-concentration ($\varkappa$ vs. c) curve. Hence, the classical theory of conductance is unable to explain even qualitatively the character of the concentration dependence of conductivity. According to this theory, the following equation must hold for equivalent conductance as a function of the solution composition:

$$\lambda_c = \alpha (\lambda_+^0 + \lambda_-^0) = \alpha \lambda_0$$

Upon dilution the degree of dissociation of an electrolyte increases, approaching unity, and the equivalent conductance must also tend to a certain limit equal to λ_0. So the general course of the equivalent conductance-concentration (λ vs. c) curve can be interpreted qualitatively from the standpoint of classical theory. From Ost-

wald's dilution law

$$K = \frac{\alpha_c^2 c}{1 - \alpha_c}$$

and relation (4.29), with $\alpha_c = \lambda_c/\lambda_0$ taken into account, it follows that at $\alpha_c \ll 1$

$$\lambda_c^2 = K\lambda_0^2 \frac{1}{c}$$

or

$$\log \lambda_c = \frac{1}{2} \log K\lambda_0^2 - \frac{1}{2} \log c \tag{5.1}$$

Expression (5.1) coincides in form with the empirical equation (4.53), which is valid for weak electrolytes. It will however be pointless to try to obtain, using the classical theory, an equation similar to the Kohlrausch empirical square root law, which holds for solutions of strong electrolytes. The classical theory of electrical conductance based on the Arrhenius theory of electrolytic dissociation can explain neither the variation of transport numbers and ionic mobilities with concentration nor the closeness of the temperature coefficients of conductance and viscosity, nor the abnormally high mobilities of hydrogen and hydroxyl ions. In contrast to the assumptions of the Arrhenius theory, electrolytic solutions cannot be regarded as ideal systems either in the state of equilibrium or when an electric current is passed through them.

5.2. INTERPRETATION OF CONDUCTANCE PHENOMENA TAKING INTO ACCOUNT INTERACTION FORCES

5.2.1. BASIC PROPOSITIONS OF THE DEBYE-ONSAGER THEORY OF CONDUCTANCE

The disparity between the classical theory of conductance and experiment stems from the fact that the theory takes no account of the forces of interaction between the particles of a solution, in the first place the forces of ion-ion and also ion-solvent interaction.

In nonequilibrium processes, in particular during the passage of a current through electrolytic solutions (electrical conduction) ionic interaction must be of a different nature than under equilibrium conditions. The conductance coefficient f_λ introduced by Bjerrum is a correction factor for interionic forces operating when a current is passed through electrolytic solutions. It differs from the activity coefficient f, which refers only to equilibrium solutions. For 1 : 1-valent electrolytes ($z = 1$), with the conductance coefficient taken into account, Eq. (4.29) should be replaced by

$$\lambda_c = \alpha_c f_\lambda (\lambda_+^0 + \lambda_-^0) \tag{5.2}$$

or

$$\alpha_c f_\lambda = \frac{\lambda_c}{\lambda_0} \tag{5.3}$$

For solutions of weak electrolytes the conductance coefficient f_λ is close to unity and the conductance ratio λ_c/λ_0 will correspond to the degree of dissociation. In the case of strong electrolytes when $\alpha = 1$

$$f_\lambda = \frac{\lambda_c}{\lambda_0} \tag{5.4}$$

The value of the conductance coefficient f_λ must be a function of concentration and can be determined by experiment. A theoretical calculation of f_λ is based on definite conceptions of the structure of solutions and on the consideration of the character of changes taking place in solutions under the influence of an externally applied electric field.

One may use the solution model suggested by Debye and Hückel, according to which each ion is surrounded by an ionic atmosphere with a charge opposite to that of the central ion. Since strong electrolytes are completely dissociated ($\alpha = 1$), all the variations of equivalent conductance with concentration are caused by the change of the interaction energy. In an infinitely dilute solution, in which the ions are so far apart that interaction forces can no longer operate between them, no ionic cloud is formed and the electrolytic solution behaves like the ideal gas system. Under these conditions the equivalent conductance of the electrolyte will reach a limiting value equal to λ_0 [1].

In fact, at any electrolyte concentration different from zero, forces arise in the solution which hamper the movement of the ions and hence decrease its equivalent conductance by values λ_i, each of which corresponds to a definite type of interaction force. On this basis, in place of Eq. (5.4) one can write

$$\lambda_c = \lambda_0 - \Sigma\lambda_i \tag{5.5}$$

where $\Sigma\lambda_i$ is the total decrease of the equivalent conductance of the solution caused by all the interaction effects that take place in real solutions. The origin of one of these effects becomes clear if one considers that under the influence of an externally applied field the central ion and the ionic cloud (as entities possessing charges equal in magnitude but opposite in sign) must move in opposite directions (Fig. 5.1). Since all the ions involved are hydrated, the central ion migrates, with a velocity v_i, not in a stationary medium but in a medium travelling in the opposite direction with a velocity v_{ia}. The

[1] Even in the absence of interionic forces λ_c and λ_0 should differ from one another because of the change in the viscosity of a solution upon transition from zero concentration to a concentration c.

frictional force is known to be proportional to the velocity of movement of a particle; for a real solution its value is given by the equation

$$_fy_r = {}_fk_i\,(v_i + v_{ia}) \tag{5.6}$$

while for an ideal solution it would be equal to

$$_fy_{id} = {}_fk_i v_i \tag{5.7}$$

where $_fk_i$ is the coefficient of internal friction.

The decrease of conductance must be proportional to the increased frictional force. If we denote by λ_I the change of the equivalent conductance of a solution resulting from this effect, then

$$\lambda_I = f\,(_fy_r) \tag{5.8}$$

or

$$\lambda_I = f\,(_fy_r - {}_fy_{id}) \tag{5.9}$$

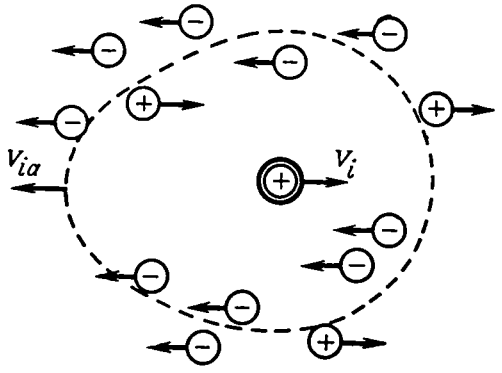

Fig. 5.1. Migration of a central ion and an ionic atmosphere in an electric field

The extra frictional force associated with the existence of an ionic cloud and its migration in a direction opposite to the movement of the central ion is known as the *electrophoretic force*; the braking effect produced by this force is termed the *electrophoretic effect.*

Another retarding effect is also associated with the presence of the ionic cloud and its influence on ionic migration. It has been found that the buildup and decay of an ionic cloud occurs at a greater but finite velocity. This velocity is characterized by the so-called *relaxation time* τ_r, which may be considered as a quantity inverse to the velocity constant of the formation or decay of the ionic cloud. Relaxation time depends on the ionic strength of a solution, its viscosity and dielectric constant and is defined by the equation

$$\tau_r = \frac{{}_fk}{kT\chi^2} \tag{5.10}$$

where $_fk$ = coefficient of internal friction of solution
k = Boltzmann constant
T = absolute temperature
χ = Debye-Hückel length.

For an aqueous solution of a 1 : 1-valent electrolyte Eq. (5.10) is simplified and the relaxation time can be calculated approximately from the equation

$$\tau_r = \frac{10^{-10}}{c} \tag{5.11}$$

where c is the concentration of the electrolyte. When the central ion is moving, a certain time elapses before the old ionic cloud is broken down and a new one is built up. For this reason there is always some excess charge of opposite sign behind the moving central ion, whose drift is thus retarded by the arising electrical forces of attraction. This retarding effect is called the *relaxation effect*. If the variation of equivalent conductance due to the relaxation effect is designated by λ_{II}, the fall in conductance upon transition from zero concentration (the ideal solution) to a concentration c will be given by the equation

$$\lambda_c = \lambda_0 - \lambda_I - \lambda_{II} \tag{5.12}$$

in which account is taken of both the electrophoretic and relaxation effects.

Debye and Hückel derived theoretical formulas for λ_I and λ_{II} containing one empirical constant. Their calculations were later improved by Onsager, who took into consideration that ions do not migrate along a straight line and that the ionic cloud is a statistical formation. The Onsager equation has the following form:

$$\lambda_c = \lambda_0 - \frac{9.9 \times 10^5}{(DT)^{3/2}} B\lambda_0 \sqrt{\Sigma \nu_i z_i^2 c} - \frac{29.1}{(DT)^{1/2}\gamma} \Sigma \nu_i z_i^2 \sqrt{\Sigma \nu_i z_i^2 c} \tag{5.13}$$

where

$$B = \frac{2g}{1+\sqrt{g}} z_1 z_2$$

and

$$g = \frac{z_1 z_2 (v_1^0 + v_2^0)}{(z_1 + z_2)(z_2 v_1^0 + z_1 v_2^0)}$$

and γ is the viscosity of the solvent.

For aqueous solutions of 1 : 1-valent electrolytes at 25°C Eq. (4.13) takes the form

$$\lambda_c = \lambda_0 - (0.224\,\lambda_0 + 50.5)\sqrt{c} \tag{5.14}$$

Equations (4.13) and (4.14) have the same form as the empirical square root law of Kohlrausch [1]. They enable one to predict the numerical value of the constant A contained in the Kohlrausch equation.

The Onsager formula is in accord with experimental data in the range of concentrations covered by the square root law. Agreement with experiment deteriorates with increasing concentration. The Onsager equation should be regarded as an equivalent of the first approximation of the Debye-Hückel theory for electrical conductance.

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[1] The cubic root law which is applicable in the range of moderate concentrations does not follow from the Onsager theory, but can be deduced from the Ghosh theory.

It therefore yields only the limiting value of conductance at an electrolyte concentration approaching zero, i.e., the limiting tangent to the conductance versus concentration curve. Similarly to the Debye-Hückel second approximation for equilibrium in electrolytic solutions, an attempt could be made to take into account the effect of the finite size of ions and introduce the parameter a into the conductance equations. Such attempts were made by Kaneko (1932), Falkenhagen (1952), Onsager and Fuoss (1955), and others. Following La Mer, Pitts (1953) also took into account the additional terms of the series expansion of the exponential function (see page 66), and Robinson and Stokes (1955) took into consideration the variation of the viscosity of a solution with concentration.

The introduction of the mean ionic diameter a (an empirical constant) and the use of an experimental value of viscosity made it possible to obtain a better fit with experiment and to extend the range of validity of the thus modified Onsager equation to the more concentrated solutions. The resulting equations however were so complicated that they had no practical value. For example, the Onsager-Fuoss equation

$$\lambda_c = \lambda_0 + B\sqrt{c} + Ec \ln c + Ic \tag{5.15}$$

contains a logarithmic term and, in addition to the constant E (determined by the same parameters as the constant B of the Onsager original equation), the quantity I, which depends on the size of the ions.

For concentrated solutions use is made of empirical formulas. One of the best is the Shedlovsky formula

$$\lambda_0 = \frac{\lambda_c + b\sqrt{c}}{1 - a\sqrt{c}} - Bc \tag{5.16}$$

where B is an empirical coefficient. The first term on the right-hand side of Eq. (5.16) corresponds to the Onsager equation (5.13), which may be written as

$$\lambda_c = \lambda_0 - (a\lambda + b)\sqrt{c} \tag{5.17}$$

or

$$\lambda_0 = \frac{\lambda_c + b\sqrt{c}}{1 - a\sqrt{c}} \tag{5.18}$$

5.2.2. WIEN EFFECT AND THE DISPERSION OF CONDUCTANCE

In 1928 Wien found that in the region of high fields the conductance of a solution increases with field strength. At first it increases slowly and then, at high field strengths, faster and, finally, reaches a certain limiting value at very high field strengths. For each particular electrolyte this limiting value corresponds to its conductance

at zero concentration irrespective of the solution concentration. For weak electrolytes Wien observed an even more pronounced rise of conductance with increasing field strength. He established the following regularity: the lower the degree of dissociation of an electrolyte, the greater is the rise of its conductance, which tends to the conductance at zero concentration.

The results obtained by Wien seemed at first quite improbable. They contradicted the widely accepted concept of the applicability of Ohm's law to electrolytic solutions. Indeed, by Ohm's law

$$\Delta\psi = RI$$

the resistance R (or conductance, the reciprocal of resistance) is a constant for a given system and consequently the field strength must depend linearly on the current intensity. But from the experiments carried out by Wien it follows that at high values of $\Delta\psi$ the resistance R is no longer constant and begins to fall with increasing field strength. Hence, the field strength does not increase proportionally to current intensity and in this case Ohm's law ceases to be valid. Some scientists believed that the Wien effect was the result of some secondary phenomena that had not been taken into account. It was supposed, for example, that the decrease of resistance at high field strengths is caused by the high temperature of the electrolyte. But calculations and further investigations with the aid of an improved technique using short-time current pulses (to rule out an appreciable rise of temperature) confirmed Wien's observation concerning the effect of the field strength on the conductance of electrolytes.

As far as strong electrolytes are concerned, the Wien effect can be explained on the basis of the Debye-Onsager theory of conductance. According to the concepts of Debye and Hückel each ion in a solution is surrounded by an ionic atmosphere of radius $1/\chi$. As long as the drift velocity of an ion is small (as compared with the rate of decay and buildup of the ionic cloud) the retardation effects associated with the ionic atmosphere are retained and the value of conductance at a given concentration is

$$\lambda_c = \lambda_0 - \lambda_I - \lambda_{II} \tag{5.19}$$

But it is known that the mobility of ions does not remain constant with increasing field strength and increases according to Eq. (4.10):

$$v_i = \frac{z_i e}{f k_i} \psi'$$

At a sufficiently high value of ψ' it may turn out that the path travelled by the ion while the old ionic cloud decays and a new one is built up, i.e., during the double relaxation time τ_r, will be equal to

or greater than the radius of the ionic atmosphere

$$2\tau_r \frac{z_i e}{f k_i} \psi' = 2\tau_r v_i^0 \psi' \geqslant 1/\chi \tag{5.20}$$

Under these circumstances the ion goes beyond the limits of its ionic cloud. A new ionic cloud will have no time to form at each new site of the ion and hence the overall retarding effect will decrease. By means of Eq. (5.20) one can estimate approximately the field strength at which the Wien effect sets in. Using Eq. (5.10) for relaxation time and substituting it into expression (5.20), one gets the following equation for the field strength being sought:

$$\psi' = \frac{1}{2} \frac{kT}{f k_i v_i^0} \chi = \frac{kT}{2ze} \chi \tag{5.21}$$

In the case of a uni-univalent electrolyte at room temperature Eq. (5.11) simplifies to:

$$\psi' = 4 \times 10^5 \sqrt{c}$$

Thus, for a 0.001*N* solution of a 1:1-valent electrolyte the Wien effect comes into operation at field strengths of the order of 10^4 V/cm, and for a 1*N* solution at 4×10^5 V/cm.

A further rise of the field strength leads to such a high drift velocity of the ions at which no ionic cloud will be able to form. All the associated retarding effects will therefore disappear. No changes of conductance either due to the electrophoretic or to the relaxation force will then be observed. In that case

$$\lambda_{\mathrm{I}} = 0, \ \lambda_{\mathrm{II}} = 0 \text{ and } \lambda_c = \lambda_0$$

The effect of the field strength on the conductance of weak electrolytes (in which the interionic forces are close to zero because of the low concentration of free ions) is probably associated with a change in the degree of dissociation under the influence of the applied field. Proceeding from this conjecture, Onsager worked out a qualitative and quantitative theory of this phenomenon. He showed that the rate of dissociation of weak electrolytes increases with field strength, whereas the rate of ionic recombination is independent of it; as a result, the degree of dissociation must increase. The percentage increase of the dissociation constant calculated by Onsager on the basis of his theory is in good agreement with the experimental observations of Wien.

Shortly after the discovery of the Wien effect, Debye and Falkenhagen predicted another effect: the conductance of electrolytic solutions increases with the frequency of the applied electric field. This effect is known as the *Debye-Falkenhagen effect* or the *dispersion of conductance*. It also depends on the presence of an ionic cloud. Indeed, at high frequencies ions do not travel in a solution but just

perform oscillatory motions in a direction parallel to the direction of the electric field. The central ion has no time to go beyond its ionic cloud, which in turn has no time to decay to any noticeable extent and at each given instant only oscillates in a direction opposite to the movement of the central ion. In this case the forces involved in the decay and formation of the ionic cloud, i.e., the retarding relaxation forces, reveal themselves to a lesser degree and the conductance of the solution increases. At high frequencies it reaches a value which differs from the conductance at infinite dilution by the amount λ_I since the relaxation effect disappears ($\lambda_{II} = 0$) and the retarding electrophoretic effect persists. In this case

$$\lambda_c = \lambda_0 - \lambda_I$$

The calculations of Debye and Falkenhagen were verified experimentally by Wien, who found them to be in good agreement with experiment.

5.2.3. THEORETICAL INTERPRETATION OF TRANSPORT NUMBERS. TRUE TRANSPORT NUMBERS

The laws governing the variation of transport numbers of ions with concentration can be accounted for on the basis of the Debye-Onsager theory of electrolytic conduction. Thus, proceeding from this theory, Stokes derived equations which correctly express the experimental dependence of transport numbers on the electrolyte concentration. He showed that if at infinite dilution the transport number of an ion, t_i^0, is equal to 0.5, it remains constant when the concentration (or ionic strength) of the solution is changed. At $t_i^0 > 0.5$ an increase in the ionic strength increases the transport number, i.e., $t_i > t_i^0$. Conversely, when $t_i^0 < 0.5$ the growth of the ionic strength leads to a decrease in the transport number, and then $t_i < t_i^0$.

The temperature dependence of transport numbers however cannot be explained merely by taking into account the forces of ionic interaction; one should also reckon with the effect of ion solvation. By considering the phenomenon of solvation one can account for the increase of the mobilities and transport numbers of cations with increasing radius observed for a series of analogous compounds. As a result of solvation, the effective sizes of moving particles of small radius are found to increase to a greater extent than those of large particles, and their movement is retarded. The fact that with rising temperature transport numbers tend to a limiting value equal to 0.5 should be linked with the process of dehydration, which intensifies with temperature and results in the levelling out of the effective ionic sizes. It is also easy to understand why the temperature coefficients of the electrical conductance and viscosity of water

coincide if one takes into account that the ions in solution are hydrated and hence their migration is hampered by the friction between the water molecules forming their hydrate shells and the surrounding water.

Since the water moves along with the ions, the transport numbers evaluated, for example, from the concentration changes in the electrode compartments, i.e., by Hittorf's method, do not correspond to their true values. Different ionic species move with different velocities and the number of water molecules moving together with them is not the same; the concentration change near the electrode is therefore the result of a decrease (or increase) not only in the number of solute particles but in the number of water molecules as well. If ion hydration is not taken into account when calculating transport numbers from concentration changes, the numbers so obtained are *apparent* (or *Hittorf*) *numbers*, and a correction must be applied to obtain the *true transport numbers* (these are also known as *Washborn transport numbers* because Washborn was the first to study this phenomenon). The apparent t_i and true T_i transport numbers are connected by the following relations (for cations and anions, respectively):

$$T_+ = t_+ + c\Delta n_{H_2O} \tag{5.22}$$

and

$$T_- = t_- - c\Delta n_{H_2O} \tag{5.23}$$

where c = initial concentration of solution

$\Delta n_{H_2O} = n_{h(+)} - n_{h(-)}$, i.e., the difference between the hydration numbers for a cation ($n_{h(+)}$) and an anion ($n_{h(-)}$) in terms of one gram-equivalent.

In order to obtain true transport numbers from apparent ones it is necessary to know the hydration numbers of the ions. But their values available at present are unreliable and cannot be used for calculations by means of Eqs. (5.22) and (5.23). To determine true transport numbers, it was suggested that, in addition to an electrolyte (whose transport numbers are to be determined), an unionized soluble indifferent substance be introduced into a solution. Since its particles have no charge, this substance is supposed to be nonconducting. In this case the change of the electrolyte concentration is determined not with respect to the solvent (water), which moves along with the ions, but to the reference substance added. This method[1)] was devised in the hope of obtaining true transport numbers and determining the difference between the hydration numbers of electrolyte ions by comparing the true numbers with apparent ones. Then, by making a more or less substantiated assumption as to the

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[1)] Proposed by Nernst.—*Tr.*

hydration number of a single ion, one could determine the hydration numbers of other ions. But such an absolutely inert substance is impossible to find. For this reason, apparent transport numbers are used at present, all the more so that precisely these numbers are of importance in determining the conditions under which many electrochemical processes take place.

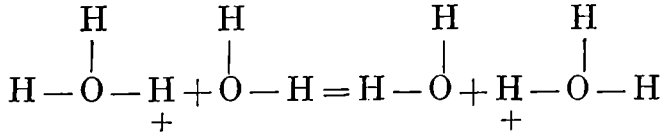
5.3. ANOMALIES IN ELECTRICAL CONDUCTANCE. SOME SPECIAL CASES OF CONDUCTION

5.3.1. THE ABNORMAL MOBILITY OF HYDROGEN AND HYDROXYL IONS

The abnormal mobilities of hydrogen and hydroxyl ions which are much higher than those of all other ions lead one to suppose that the movement of these ions in aqueous solutions obeys a special mechanism of migration. The modern theory of the abnormal mobility of hydrogen and hydroxyl ions developed by Bernal and Fowler is an extension of the idea of the mechanism of conduction in ionic solutions suggested by Grotthus at the beginning of last century (1806).

Since the greater part of the hydration energy of a proton is evolved when it unites with the first water molecule, it is thought that in aqueous solutions the hydrogen ion must be present in the form of the hydroxonium (or hydronium) ion H_3O^+. The proton can migrate from one water molecule to the next. These proton transfers involve a certain amount of activation energy. In the absence of an external field proton jumps may occur in any direction with equal probability. In the presence of an external field the probability of proton migration in the direction of the field increases (since the activation energy in this direction diminishes), and the process of proton movement will occur by a chain mechanism, i.e., the proton will be passed on from one water molecule to the next and so on—a passing-the-proton game:

the direction of the field →

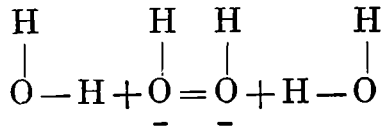


the direction of proton transfer →

As follows from the scheme, the orientation of the water molecule after the proton has left the hydroxonium ion is unfavourable for the next proton jump, a circumstance that lowers the rate of proton transfer which otherwise would have been still higher.

The abnormal mobility of the hydroxonium ion may be represented in a similar way:

the direction of the field →



the direction of movement of the hydroxyl ion ←

The energy required to pull the proton away from the hydroxyl radical OH^- in a water molecule is higher than that needed to tear the hydrogen ion H^+ off the water molecule in a hydroxonium ion. So the probability of proton jumps and hence the velocity of movement of hydroxyl ions must be lower as compared with hydrogen ions. The unfavourable orientation of the water molecule formed also adds to the spatial difficulties for the next proton jump, as a result of which the rate of transfer of hydroxyl ions is lowered.

5.3.2. THE ANOMALOUS CONDUCTANCE OF NONAQUEOUS ELECTROLYTE SOLUTIONS

For aqueous solutions of most electrolytes the change of equivalent (or molar) conductance with dilution is expressed by a smooth curve (see Fig. 4.5). The conductance of an electrolyte increases with dilution, tending in the limit to the conductance value at infinite dilution. A fundamentally different shape of the molar conductance-dilution (λ vs. V) curve was observed by Kablukov in 1890 while studying the properties of hydrogen chloride solutions in amyl alcohol. He found that in a definite range of concentrations the conductance of a solution does not rise but decreases with dilution. These studies were later continued by many researchers, who confirmed Kablukov's observations. It turned out that when solutions with a low dielectric constant are used, then, instead of a monotonic conductance-dilution curve typical of aqueous solutions, curves with a minimum are obtained, the minimum being followed by a gradual rise. One may occassionally find both a maximum and a minimum on λ vs. V or λ vs. c curves, i.e., the concentration dependence of conductance here is more complicated than in aqueous solutions.

The variation of molar (or equivalent) conductance with dilution, characterized by the appearance of extrema on the λ vs. V curve, corresponds to "anomalous conduction". This phenomenon was observed by Sakhanov for solutions of silver nitrate in some nonaqueous pure and mixed solvents possessing low dielectric constants. These observations were confirmed by Walden, who was the first to use, as an electrolyte, tetrasubstituted ammonium salts (so-called

Walden salts), which are readily soluble in most nonaqueous solvents. A detailed study of anomalous conduction in solvents consisting of a dioxan-water mixture was carried out by Fuoss and Kraus.

Sakhanov also paid attention to the fact that in concentrated solutions the conductance value being measured included the viscosity effect. Therefore he introduced the concept of *corrected conductance* λ_{cor}, i.e., the value of equivalent conductance in which account is taken of an increase in the viscosity γ at a given dilution compared with the viscosity γ_∞ at infinite dilution:

$$\lambda_{cor} = \lambda \frac{\gamma}{\gamma_\infty} \tag{5.24}$$

Corrected conductance is more sensitive to changes in the solution composition than the ordinary value of conductance, uncorrected for viscosity. In a comparative study of the conductance of electrolytes in different solvents one should take into account the effect of the viscosity of the medium.

The classical theory of conductance and the Debye-Onsager theory are unsuitable for interpreting the phenomena of anomalous conductance. Neither can equivalent conductance-dilution curves with extrema be obtained by considering the solvation effect. The theory of anomalous conductance was first formulated by Sakhanov in the period 1913-16 on the basis of the concepts of electrolyte association which manifests itself most distinctly in solvents with low dielectric constants and leads to the formation of complex molecular and ionic substances. According to Sakhanov, in addition to electrolyte molecules MA, concentrated solutions contain associated molecules $(MA)_x$, which are in equilibrium with simple molecules:

$$x\mathrm{MA} = (\mathrm{MA})_x \tag{5.25}$$

Associated molecules are capable of dissociating into complex ions—current carriers—under the given conditions

$$(\mathrm{MA})_x = \mathrm{M}_x^+ + \mathrm{A}_x^- \tag{5.26}$$

When solutions are diluted, the equilibrium of the reaction (5.25) is shifted to the left. The number of complex molecules dissociating into ions according to Eq. (5.26) is reduced and consequently the conductance of the solution falls. Upon further dilution, when more and more electrolyte appears in the solution as simple molecules, their dissociation into simple ions begins to play an appreciable role

$$\mathrm{MA} = \mathrm{M}^+ + \mathrm{A}^- \tag{5.27}$$

and the conductance will again increase according to the law which usually obtains for the variation of equivalent conductance with dilution. If it is assumed that a solution contains molecules of diffe-

rent degree of association and also the corresponding complex ions, one can then account for the still more complicated variation of conductance with dilution when, in addition to a minimum, a maximum or several maxima and minima appear on the curve. Sakhanov deduced an equation for the dependence of λ on V which is in qualitative agreement with the shape of the experimental anomalous-conductance curves.

The concepts worked out by Sakhanov were substantially extended and developed in later investigations. Thus, Semenchenko (1923-24) and Bjerrum (1926-27) showed that ion pairs M^+A^- may form in concentrated solutions of electrolytes in water (and—in nonaqueous solvents with low dielectric constants—at moderate electrolyte concentrations as well). Ion pairs consisting of positive and negative ions are formed under the action of purely coulombic forces; they are therefore not so strong as undissociated electrolyte molecules. The bond holding the ions together however is strong enough for the original ions to lose their independence and display properties (mobility, etc.) characteristic of uncharged particles. The appearance in a solution of ion pairs in addition to simple molecules must lead to a more rapid decrease in molar conductance with increasing concentration, this fall being the more pronounced the lower the dielectric constant of the solvent.

The effect of the solvent nature on the dissociation (and association) of solutes and on their conductance and diffusion can be better understood if the nature of the bonds existing between the particles of these substances in their original state, i.e., in their "pure" form, is taken into account. From this point of view all substances may be divided into two extreme groups. The first group includes compounds with a crystal lattice built up of separate ions. It would hardly be correct to use the term "electrolytic dissociation" to describe the behaviour of these substances during dissolution because they do not contain any undissociated molecules from the very outset; in this case dissociation equilibrium in the Arrhenius sense has no physical meaning. Such substances are known as *ionophores* (i.e., *true electrolytes*); potassium chloride is a typical ionophore. For dissolved ionophores, say, for KCl, it is more correct to write, instead of a dissociation reaction with the participation of nonexistent molecules of KCl, the following reaction of association

$$K^+ + Cl^- = K^+Cl^-$$

leading to the formation of ion pairs from the original single ions.

Here the effect of a solvent, say of its dielectric constant, should be first of all associated with the reaction of association rather than dissociation[1]. In water, which is a solvent possessing a high die-

[1] Hydration is in this case a source of energy for the breakdown of the lattice and not for the dissociation of molecules.

lectric constant, ion-pair formation is not very likely since the energy of coulombic attraction between ions is small compared with the thermal energy kT. That is why in water all ionophores become strong electrolytes and are present as independent hydrated ions. When nonaqueous solvents of lower dielectric constant are used, the equilibrium of ion association is shifted to the right. This shift of the equilibrium reduces the number of single ions, increases the probability of formation of ion pairs and of more complex ions (see below), lowers the conductance and gives rise to "anomalous" conduction.

To the second group belong substances consisting of aggregates of molecules, i.e., of neutral uncharged particles. The formation of ions on dissolution of such substances and hence the conduction of current by these ions is possible owing to chemical interaction with the solvent. These substances are called *ionogens* (i.e., *potential electrolytes*). Acetic acid is a typical example of an ionogen. The process of ion formation on dissolution of acetic acid in water, for example, can be described as follows:

(1) acetic acid reacts with the solvent to form a molecular complex

$$CH_3COOH + H_2O = CH_3COOH \cdot H_2O$$

(2) the resulting molecular complex is transformed into an ion pair as a result of intramolecular rearrangement

$$CH_3COOH \cdot H_2O = CH_3COO^- \cdot H_3O^+$$

(3) the ion pair dissociates into free ions

$$CH_3COO^- \cdot H_2O^+ = CH_3COO^- + H_3O^+$$

The equilibrium of the last reaction is shifted, as a rule (except for very dilute solutions), to the left. Ionogens in aqueous solutions are therefore weak electrolytes and poor conductors of electricity.

According to the Fuoss-Kraus approach (1934-35), in concentrated solutions, besides uncharged ion pairs, there may also form triple ions, in which the ionic charges do not cancel

$$M^+A^- + A^- = MA_2 \qquad (5.28)$$

$$M^+A^- + M^+ = M_2A^+ \qquad (5.29)$$

Triple-ion formation may also be treated as the result of the association of two ion pairs with subsequent ionization of the complexes formed

$$M^+A^- + M^+A^- = (M^+A^-)_2 = MA_2^- + M^+ \qquad (5.30)$$

and

$$M^+A^- + M^+A^- = (M^+A^-)_2 = M_2A^+ + A^- \qquad (5.31)$$

The concept of triple ions allows one to account for the appearance of a minimum on the equivalent conductance-dilution curve. Indeed,

at high dilutions a solution contains only simple electrolyte molecules and the corresponding simple ions. With increasing concentration the equivalent conductance falls because the equilibrium between the ions and the molecules, described by Eq. (5.27) for the indicated dilution range, must shift to the left, i.e., towards the undissociated molecules. As the concentration continues to increase the formation of triple ions by reactions (5.30) and (5.31) becomes possible, and the electrical conductance will begin to increase as a result of their direct participation in the conduction of the current. Proceeding from these considerations, Fuoss and Kraus derived an equation for the dependence of equivalent conductance on the electrolyte concentration

$$\lambda_c = \text{const}_1\, c^{-1/2} + \text{const}_2\, c^{1/2} \qquad (5.32)$$

The constants of Eq. (5.32) depend on the equilibrium constants of the reactions (5.27), (5.28) and (5.29) and on the limiting values of equivalent conductance at zero concentrations of particles MA, MA_2^- and M_2A^+. Equation (5.32) describes a curve with a minimum; it can be shown that the concentration corresponding to the lowest conductance value can easily be determined if the equilibrium constants of the reaction of triple-ion formation and the values of their limiting conductance are known.

When nonaqueous solvents of low dielectric constant are used, the difference between ionophores and ionogens is not so distinct. In both cases chemical interaction between solvent and solute acquires special significance. For instance, in liquid ammonia the conductances of potassium chloride and acetic acid (the latter being present as ammonium acetate) are found to be close both in magnitude and in the character of variation with concentration of the solute.

In order to account for the appearance of a maximum on the conductance curve frequently observed with concentrated nonaqueous electrolyte solutions it is necessary to assume, following Sakhanov, that, along with charged triple ions, there also exist uncharged associated compounds. These compounds may result, for example, from the following reaction

$$M_2A^+ + MA_2^- = (MA)_3 \qquad (5.33)$$

The presence in solutions of this kind of both charged and uncharged associated particles has been verified experimentally. The influence of such complexes on the properties of electrolyte solutions is not confined to the phenomena of ionic conduction. It should also be taken into account in considering equilibrium in electrolytic solutions. The formation of ion pairs, triple ions and uncharged complexes must also affect the course of other processes (e.g., diffusion) taking place in electrolytic solutions.

Thus, under given conditions of temperature and pressure the electrical conductance of any system consisting of a solute and a solvent is governed by the following factors: (1) the nature of chemical bonds between the solute particles in their original state; (2) the character of solvent-solute interaction; (3) the dielectric constant of the solvent; and (4) the viscosity of the solution. The last two factors are especially important in the case of inert solvents. As shown by Fialkov (1965-66), a linear relationship is observed here between the logarithm of the product of viscosity by conductance and the quantity inverse to the dielectric constant of the solution. He found that if the ratio of the viscosity of an electrolyte to that of the solvent exceeds a certain critical value, a maximum appears on the conductivity-concentration curve.

5.3.3. THE CONDUCTANCE OF SOLUTIONS OF SOME METALS IN LIQUID AMMONIA

Curves similar to the curves of the anomalous conductance of electrolytes in nonaqueous organic solvents were obtained in studying solutions of alkali and alkaline-earth metals in liquid ammonia. On the curve of the molar conductance of a solution of potassium in liquid ammonia (Fig. 5.2) there is a minimum at a definite degree of dilution. The conductance then increases regularly with dilution, approaching a certain limiting value. Using a formal analogy between the anomalous conductance and the conductance of solutions of metals in liquid ammonia, one could make an attempt to apply the concepts of ion-complex formation to this case as well. But the conductance of solutions of metals in liquid ammonia is so high that the ions (both simple and complex) are incapable of providing it. These interesting solutions differ considerably in their nature from solutions of electrolytes in water or in organic solvents.

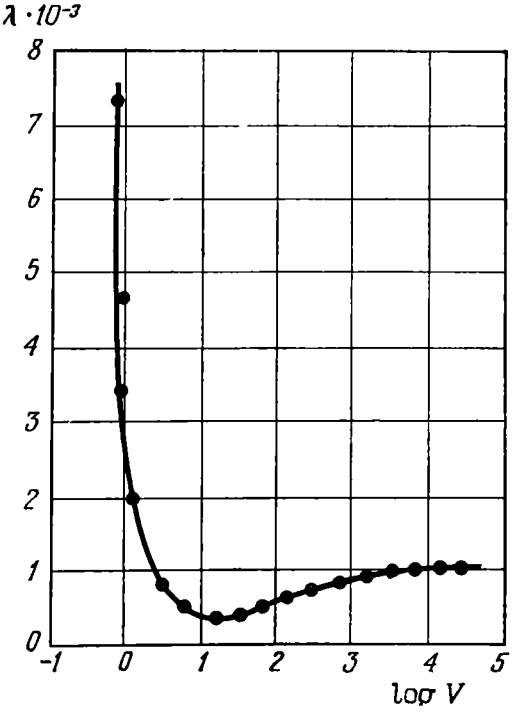


Fig. 5.2. Dilution dependence of the molar conductance of a potassium solution in liquid ammonia

Liquid ammonia is a solvent resembling water in some respects. The intrinsic conductance of water is known to manifest itself as

a result of its dissociation according to the equation

$$2H_2O = H_3O^+ + OH^- \tag{5.34}$$

and its dissociation constant at ordinary temperatures is close to 10^{-14}. An equilibrium similar to (5.34) is also observed in liquid ammonia

$$2NH_3 = NH_4^+ + NH_2^- \tag{5.35}$$

But the equilibrium constant of this reaction at —33°C is around 10^{-33} (according to Monoszon and Pleskov), which is many orders lower than the dissociation constant of water. The intrinsic conductance of liquid ammonia is therefore markedly lower than that of water. Like water, liquid ammonia is capable of dissolving considerable amounts of alkali metals. For example, at —33.7°C one gram-atom each of lithium, sodium and potassium dissolves in 3.7, 5.5 and 5.0 moles of liquid ammonia, respectively. But, in contrast to water, the dissolution of alkali metals in liquid ammonia is not accompanied by the decomposition of the solvent and the evolution of gaseous hydrogen. On the basis of these and some other data, the process of dissolution of alkali metals in liquid ammonia can be described by the following equation

$$M + xNH_3 = [M(NH_3)_y]^+ + e\,(x - y)NH_3 \tag{5.36}$$

Hence the passage of a current through such solutions is provided by metal ions and electrons solvated by ammonia. Equation (5.36) accounts for the experimentally observed change of electrical conductance with dilution. For near-saturated solutions the degree of solvation of ions and electrons is negligibly small ($x \to 0$). The electrons in such solutions behave as free electrons in metals and their conductance must be only slightly different from the conductance of metals. The specific conductance of a saturated solution of potassium in liquid ammonia is 0.5×10^4 ohm^{-1}·cm^{-1}. This value is comparable with the conductivity of a metallic conductor such as mercury (1×10^4 ohm^{-1}·cm^{-1}). At the same time the maximum conductivity of an aqueous solution of sulphuric acid, one of the best ionic conductors, is only 0.7 ohm^{-1}·cm^{-1}, i.e., is almost four orders lower than the conductivity of a saturated solution of potassium in liquid ammonia. With dilution the degree of solvation of electrons increases (x rises), their mobility is considerably reduced and the conductance of the solution falls abruptly. At still higher dilutions the degree of solvation ceases to change, but the degree of dissociation continues to increase, which results in an increase in the molar conductance. The limiting value of molar conductance at infinite dilution is several times as high as the molar conductance of aqueous solutions of electrolytes under the same conditions. Such a high conductance may be attributed to the specificity of

anions (solvated electrons), for which the Grotthus chain mechanism of ionic migration is even more probable than for protons, and also to the lower viscosity of liquid ammonia as compared with water. So the conductance of solutions of metals in liquid ammonia is a special case of mixed electronic and ionic conduction. The relative share of electronic and ionic conduction may vary within wide limits depending on the composition of the solution.

5.3.4. SOME OTHER SYSTEMS EXHIBITING MIXED CONDUCTION

Solutions of metals in liquid ammonia are not the sole conductors exhibiting mixed conduction. This group also includes gases subjected to the action of either an electric discharge or radioactive radiation or heated to very high temperatures. The majority of solid salts exhibit ionic conduction of the unipolar type, i.e., the current is carried by only one ionic species. For example, in crystals of a silver halide the current is carried only by cations and hence the transport number of a silver ion is unity, while that of a halide anion is equal to zero. Conversely, in crystals of lead nitrate the transport number of the cation is zero and only nitrate ions are mobile in an electric field. With increasing temperature, however, almost all solid salts show electronic conduction. They thus become conductors often of the semiconductor type, exhibiting mixed electronic and ionic conduction. For some solid compounds, say for α-Ag_2S, mixed conduction is observed over a wide temperature range. Typical first-class conductors such as amalgams and metallic alloys (especially in molten state) show slight ionic conduction when heavy currents are passed through them, one of the alloy components being transported to the cathode and the other to the anode. The phenomenon of current transport by ions in amalgams and alloys has been studied insufficiently so far.

CHAPTER 6

Diffusion in Electrolyte Solutions

6.1. BASIC LAWS OF MOLECULAR DIFFUSION

6.1.1. DERIVATION OF FICK'S LAWS

Diffusion occurs as a result of the inhomogeneity of the system, i.e., when its separate parts contain either different substances or the same substances but in different concentrations (this gives rise to a concentration gradient). The transport processes of diffusion can be expressed quantitatively with the aid of Fick's laws.

Suppose we have a tube of cross section Ω filled with a solution of some substance (Fig. 6.1) the concentration of which decreases in the direction of the x-axis. If in this tube we mentally isolate

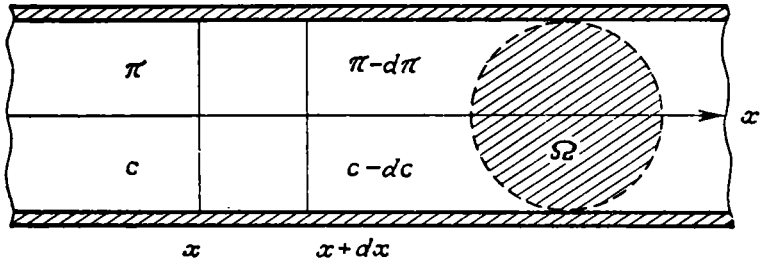


Fig. 6.1. The diffusion process (schematic)

an elementary layer enclosed between x and $x + dx$ (its thickness being dx and volume $\Omega\, dx$), then the concentration and osmotic pressure will be, respectively, c and π on its left and $c - dc$ and $\pi - d\pi$ on its right. As a result, the elementary layer will be acted upon (along the x-axis) by an excess force $\Omega\, d\pi$ and each particle in the layer $\Omega\, dx$ by an excess force equal to

$$-\frac{\Omega\, d\pi}{cN_A \Omega\, dx} = -\frac{d\pi}{cN_A\, dx} \tag{6.1}$$

Under the action of osmotic pressure the particles must move along the x-axis with a velocity ω given by the equation

$$\omega_f k = -\frac{d\pi}{cN_A\, dx} \tag{6.2}$$

where ${}_fk$ is the coefficient of internal friction.

Assuming that the ideal gas laws are applicable to the solution in question and expressing $d\pi$ in terms of $RT\,dc$, one can rewrite Eq. (6.2) as follows:

$$\omega_f k = -\frac{RT}{cN_A} \cdot \frac{dc}{dx} \tag{6.3}$$

The number of particles crossing the section Ω in time dt is

$$dn = \omega \Omega c N_A \, dt \tag{6.4}$$

or, after eliminating ω,

$$dn = -\frac{RT}{f k} \Omega \frac{dc}{dx} dt \tag{6.5}$$

Denoting the quantity $RT/_f k$ by Δ, one gets

$$dn = -\Delta \Omega \frac{dc}{dx} dt \tag{6.6}$$

Equation (6.6) is known as *Fick's first law*. The coefficient Δ, called the *diffusion coefficient*, or *diffusivity*[1], has the dimensions of $cm^2 \cdot sec^{-1}$ and indicates the number of particles that diffuse through a unit cross-sectional area (1 cm^2) of the solution per 1 sec.

In deducing Fick's first law it was assumed that the concentration gradient does not change with time and is independent of the value of x. Fick's first law is thus applicable to the process of steady-state diffusion. Diffusion however does not necessarily occur under steady-state conditions. For example, if the left-hand portion of the tube contains a solid capable of dissolving in the liquid filling the tube, the concentration of the solution will change both in space and in time. It will increase and reach a limiting value corresponding to the solubility of the substance, and the front of the saturated solution will move from left to right.

The number of particles that will enter the elementary layer dx during the time dt is given by

$$dn = -\Delta \Omega \frac{dc}{dx} dt$$

The number of particles that will leave the layer during the same time dt is

$$dn' = \Delta \Omega \left[\frac{dc}{dx} + \frac{d}{dx} \left(\frac{dc}{dx} \right) dx \right] dt$$

since the concentration gradients at the right and left boundaries of the layer differ by the amount $(d/dx)\,(dc/dx)\,dx$. Therefore the num-

[1] When referred to molar quantities diffusivity will be smaller by a factor of N_A, i.e.,

$$\Delta = \frac{RT}{{}_f k N_A} = \frac{kT}{{}_f k}$$

ber of particles retained in the layer dx will be

$$dn - dn' = \Delta\Omega \left(\frac{\partial^2 c}{\partial x^2}\right) dx\, dt$$

but

$$\frac{dn - dn'}{\Omega\, dx} = \frac{dn - dn'}{dV} = dc$$

and

$$\left(\frac{\partial c}{\partial t}\right)_x = \Delta \left(\frac{\partial^2 c}{\partial x^2}\right)_t \tag{6.7}$$

Equation (6.7) is the general differential equation for the process of diffusion and serves as a mathematical expression of Fick's second law.

6.1.2. APPLICATION OF FICK'S LAWS TO ELECTROLYTE SOLUTIONS

Since in deriving Fick's laws no assumptions were made as to the nature of the solute, these laws can equally be used to describe the diffusion of electrolytes. Thus, using Eq. (6.3), one can write for the diffusion velocities ω_+ and ω_- of positive and negative ions, respectively,

$$\omega_+ = -\frac{RT}{fk_+c_+N_A} \cdot \frac{dc_+}{dx} \tag{6.8}$$

and

$$\omega_- = -\frac{RT}{fk_-c_-N_A} \cdot \frac{dc_-}{dx} \tag{6.9}$$

According to Eq. (4.13)

$$v_+^0 = \frac{z_+F}{fk_+N_0}$$

and

$$v_-^0 = \frac{z_-F}{fk_-N_0}$$

which in combination with Eqs. (6.8) and (6.9) yield the velocities of diffusing ions

$$\omega_+ = -\frac{RTv_+^0}{z_+F} \cdot \frac{1}{c_+} \cdot \frac{dc_+}{dx} \tag{6.10}$$

and

$$\omega_- = -\frac{RTv_-^0}{z_-F} \cdot \frac{1}{c_-} \cdot \frac{dc_-}{dx} \tag{6.11}$$

In accordance with Eqs. (6.6), (6.10), and (6.11) the number of positive gram-ions diffusing through the cross-sectional area Ω in

time dt is equal to

$$dn_+ = \omega_+ c_+ \Omega\, dt = -\frac{RT}{z_+ F} v_+^0 \Omega \frac{dc_+}{dx}\, dt \tag{6.12}$$

and, accordingly, the number of negative gram-ions

$$dn_- = \omega_- c_- \Omega\, dt = -\frac{RT}{z_- F} v_-^0 \Omega \frac{dc_-}{dx}\, dt \tag{6.13}$$

From expressions (6.12), (6.13), and (4.21) it follows that

$$\Delta_+ = \frac{RT}{z_+ F} v_+^0 = \frac{RT}{z_+ F^2} \lambda_+^0 \tag{6.14}$$

and

$$\Delta_- = \frac{RT}{z_- F} v_-^0 = \frac{RT}{z_- F^2} \lambda_-^0 \tag{6.15}$$

where Δ_+ and Δ_- are the diffusion coefficients of cations and anions; these coefficients have the same dimensions as the diffusion coefficient Δ ($cm^2 \cdot sec^{-1}$).

In a general case the mobilities of cations and anions are not equal ($\lambda_+^0 \neq \lambda_-^0$) and hence their diffusion coefficients are not equal either ($\Delta_+ \neq \Delta_-$). Therefore, at the same concentration gradient positive and negative ions diffuse with different velocities. Suppose that there is a boundary between two solutions of hydrochloric acid whose concentrations are, respectively, c and $c - dc$; then more hydrogen than chloride ions will diffuse in a certain time to the low-concentration side since $\lambda_{H^+}^0 > \lambda_{Cl^-}^0$. As a result, an electric potential gradient (a potential difference) develops between the high- and low-concentration sides, the dilute solution being positively charged in this case[1]. This potential difference will retard the faster hydrogen ions and accelerate the slower chloride ions. As the electric potential gradient increases both types of ions will begin to move at the same velocity and the diffusion of the electrolyte will occur in the same way as the diffusion of undissociated molecules. The stationary potential difference set up inside the solution due to the differences between ionic mobilities is called the *diffusion potential* ψ_d.

Thus, the diffusion of an electrolyte in solution arises as a result of the operation of two gradients: the concentration gradient and the electric potential gradient associated with the diffusion potential. On this basis one can write for the velocities of positive and negative ions:

$$\omega_+ = -\frac{RT}{z_+ F} \cdot \frac{v_+^0}{c_+} \cdot \frac{dc_+}{dx} - v_+^0 \frac{d\psi_d}{dx} \tag{6.16}$$

$$\omega_- = -\frac{RT}{z_- F} \cdot \frac{v_-^0}{c_-} \cdot \frac{dc_-}{dx} + v_-^0 \frac{d\psi_d}{dx} \tag{6.17}$$

[1] In all cases the dilute solution will acquire the charge carried by the more mobile ion.

or

$$\omega_+ = -\frac{v_+^0}{z_+F}\left(\frac{RT}{c_+}\cdot\frac{dc_+}{dx} + z_+F\,\frac{d\psi_d}{dx}\right) \tag{6.18}$$

$$\omega_- = -\frac{v_-^0}{z_-F}\left(\frac{RT}{c_-}\cdot\frac{dc_-}{dx} - z_-F\,\frac{d\psi_d}{dx}\right) \tag{6.19}$$

where $d\psi_d/dx$ is the electric potential gradient corresponding to the diffusion potential ψ_d. In a steady-state diffusion process at equal ionic charges ($z_+ = z_- = z$) and concentrations ($c_+ = c_- = c$) the velocities of cations and anions are also equal, ($\omega_+ = \omega_-$); therefore

$$zF\,\frac{d\psi_d}{dx} = \frac{RT}{c}\cdot\frac{v_-^0 - v_+^0}{v_+^0 + v_-^0}\cdot\frac{dc}{dx} \tag{6.20}$$

Since $\omega_+ = \omega_-$, the value of $zF\,d\psi_d/dx$ can be substituted into any one of the equations for ionic velocity, for example, into Eq. (6.17); this substitution yields an expression for the velocity of the electrolyte as a whole

$$\omega = -\frac{v_+^0}{zF}\left(\frac{RT}{c}\cdot\frac{dc}{dx} + \frac{RT}{c}\cdot\frac{v_-^0 - v_+^0}{v_+^0 + v_-^0}\cdot\frac{dc}{dx}\right) \tag{6.21}$$

or

$$\omega = -\frac{2v_+^0 v_-^0}{zF\,(v_+^0 - v_-^0)}\cdot\frac{RT}{c}\cdot\frac{dc}{dx} \tag{6.22}$$

The number of diffusing moles is equal to

$$dn = \omega\Omega c\,dt$$

and, consequently,

$$dn = -\frac{2v_+^0 v_-^0}{zF\,(v_+^0 + v_-^0)}\,RT\Omega\,\frac{dc}{dx}\,dt \tag{6.23}$$

where

$$\frac{2v_+^0 v_-^0}{zF\,(v_+^0 + v_-^0)}RT = \Delta_{elt} \tag{6.24}$$

represents the total diffusion coefficient of the electrolyte.

Combining the equation of the total diffusion coefficient of the electrolyte, Δ_{elt}, with the formulas for the diffusion coefficients of positive and negative ions, Δ_+ and Δ_-, one can express the diffusion coefficient of the electrolyte in terms of the diffusivities of its constituent ions. For binary electrolytes

$$\Delta_{elt} = \frac{2\Delta_+\Delta_-}{\Delta_+ + \Delta_-} \tag{6.25}$$

or for any type of electrolyte

$$\Delta_{elt} = \frac{(z_+ + z_-)\,\Delta_+\Delta_-}{z_+\Delta_+ + z_-\Delta_-} \tag{6.26}$$

For practical calculations of the diffusivity of an ionic species i, Δ_i, the following formulas can be used:

$$\Delta_i = 8.96 \times 10^{-10} T \frac{\lambda_i^0}{z_i}, \quad \text{cm}^2 \cdot \text{sec}^{-1} \tag{6.27}$$

or

$$\Delta_i = 7.74 \times 10^{-5} T \frac{\lambda_i^0}{z_i}, \quad \text{cm}^2 \cdot \text{day}^{-1} \tag{6.28}$$

The diffusion coefficients of some ions at 25°C calculated by Eq. (6.27) are presented in Table 6.1.

TABLE 6.1

The Diffusion Coefficients of Some Individual Ions

Ion	$\Delta_+ \times 10^5$, $\text{cm}^2 \cdot \text{sec}^{-1}$	Ion	$\Delta_- \times 10^5$, $\text{cm}^2 \cdot \text{sec}^{-1}$
H^+	9.34	OH^-	5.23
Li^+	1.04	Cl^-	2.03
Na^+	1.35	CH_3COO^-	1.09
K^+	1.98	SO_4^{2-}	1.08
Pb^{2+}	0.98	CrO_4^{2-}	1.07
Cu^{2+}	0.72		
Ni^{2+}	0.69		
Zn^{2+}	0.72		

The diffusion coefficient of a 1 : 1-valent electrolyte can be conveniently calculated from the formula

$$\Delta_{elt} = 0.154 \frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0} T, \quad \text{cm}^2 \cdot \text{day}^{-1} \tag{6.29}$$

TABLE 6.2

The Diffusion Coefficients of 1 : 1-valent Electrolytes at 18°C

Electrolyte	Δ_{elt} (exp.)	Δ_{elt} (cal.)
LiCl	1.000	0.949
NaCl	1.170	1.173
KCl	1.466	1.460
KOH	1.903	2.109
HCl	2.324	2.431
CH_3COOH	0.930	1.368

obtained from Eq. (6.24) by substituting the numerical values of the constant quantities and using the day (24 hours) as the time unit.

The diffusion coefficients of 1 : 1-valent electrolytes calculated from Eq. (6.29) and the respective experimental values are given in Table 6.2. It was assumed in calculations that the degree of dissociation of the electrolytes is unity. The agreement between the theoretical and experimental values is fairly good; an exception is acetic acid because of its low degree of dissociation.

6.2. ION-ION INTERACTION DURING THE DIFFUSION OF ELECTROLYTES

The values of diffusion coefficients given above refer to infinitely dilute solutions of electrolytes and are thus "ideal" coefficients of diffusion. The experimental values of diffusion coefficients do not remain constant as the concentration changes and decrease with increasing concentration, as a rule. Data on the concentration dependence of Δ_{elt} for some electrolytes are listed in Table 6.3. For

TABLE 6.3

The Concentration Dependence of Diffusion Coefficients at 25°C

Electrolyte	Diffusion coefficients at a concentration of, mole/1000 g solvent								
	0.000	0.001	0.005	0.01	0.05	0.1	0.5	1.0	4.0
HCl	3.339	—	—	—	3.073	3.050	3.184	3.436	5.77
LiCl	1.368	1.345	1.323	1.312	1.280	1.267	1.278	1.302	—
$CaCl_2$	1.336	1.240	1.179	—	1.121	1.110	1.140	1.203	—
$(NH_4)_2SO_4$	1.527	—	—	—	0.802	0.825	0.938	0.011	1.135
$ZnSO_4$	0.849	0.748	0.705	—	—	—	—	—	—
$LaCl_3$	1.244	1.175	1.105	—	—	—	—	—	—

most electrolytes the variation of the diffusion coefficient Δ_{elt} with concentration is expressed by a curve with a minimum.

The concentration dependence of the diffusion coefficient of an electrolyte is attributed to the forces of interaction between diffusing ions, the hydration phenomena taking place in the electrolyte and the increase (or decrease) of the viscosity of the solution. None of these effects were taken into account in the Nernst theory of electrolyte diffusion on which all the above equations are based.

In considering the effect of interionic forces on the diffusion of electrolytes one should take into account the specific nature of the diffusion process. Diffusion differs from electrical conduction in that positive and negative ions move in the same direction, whereas under the effect of a current they move in opposite directions. Furthermore, when a steady state is reached all the ions of an electrolyte diffuse at the same velocity, while under the influence of an electric

current they move independently of one another with different velocities. In view of this, the electrophoretic and relaxation forces associated with the ionic cloud reveal themselves during the diffusion of electrolytes differently than in the case of electrical conduction. In a solution at equilibrium all the ions are in a state of random motion in which the central ion and the ions belonging to the ionic cloud may move either in the same or in opposite directions. If diffusion is regarded as a process associated with slight deviations from the equilibrium state, then, in contrast to the Nernst theory, the difference of real chemical potentials, rather than the drop of osmotic pressure, should be looked upon as one of its driving forces. Another force is identified, as in the Nernst theory, with the electric field set up during the movement of oppositely charged ions migrating with different initial velocities. The need to use real chemical potentials calls for introducing the activity coefficients of electrolyte ions into the diffusion equations. The diffusion coefficient Δ for a real solution is related to the Nernst diffusion coefficient Δ^0 as follows

$$\Delta = \Delta^0 \left(1 + \frac{d \ln cf_{\pm}}{d \ln c}\right) \tag{6.30}$$

Equation (6.30) agrees satisfactorily with experiment for dilute solutions, especially for electrolytes of low valency. Its agreement with experimental data becomes worse in the case of stronger solutions and polyvalent electrolytes. The best fit between theory and experiment can be obtained if the following factors are taken into account: (1) the modified electrophoretic and relaxation effects; (2) the transport of water molecules by diffusing ions; (3) the movement of water molecules in the direction opposite to diffusion; and (4) the variation of viscosity with concentration.

The difference between the process of diffusion, on the one hand, and electrical conduction and the equilibrium state of electrolytes, on the other, must lie in the character of the ion-ion interaction. It would therefore be wrong to use the activity coefficient f or the conductance coefficient f_λ as a correction factor in considering diffusion. In this case it is necessary to introduce a special coefficient f_d, which would take into account the forces of ionic interaction specifically for the process of diffusion. This coefficient may be termed the interaction diffusion coefficient. It can be determined from the equation

$$\Delta = \Delta^0 f_d \tag{6.31}$$

In computing the value of f_d one should reckon with the specific nature of diffusion processes. As already noted, during the diffusion of electrolyte solutions the ions move in a single common direction and acquire the same velocity when steady-state diffusion sets in. Thus, the motion of oppositely charged ions largely loses its specific

nature, which is inherent in them in an equilibrium solution and is retained when an electric current is passed through it. The loss by the ions of their ability to move independently is to a certain degree equivalent to the formation of ion pairs or larger clusters of ions. The ion-pair concept is usually used in considering the properties of electrolytes in the region of high concentrations. It does not extend to the region of dilute solutions, for which the behaviour of electrolytes is satisfactorily described on the basis of the Debye-Hückel concepts of the ionic cloud. In the case of the diffusion of electrolytes, however, when the central ion and the ionic cloud move in the same direction, the central ion-ionic cloud system may be treated as a special case of ion pair with an interionic distance equal to the radius of the ion cloud, $1/\chi$. The ionic cloud may here be identified with a particle situated at the indicated distance from the central ion, moving along with it in the direction of diffusion and bearing a charge opposite in sign and equal in magnitude to the charge carried by the central ion. V. Kiryanov (1961) examined the concentration dependence of the diffusion coefficient, using the ion-pair concept. After certain simplifications the basic equation obtained by him can be put down in the form:

$$\Delta = \Delta^0 (1 - A \sqrt{c} + Bc) \tag{6.32}$$

where c = molar concentration
A and B = complex coefficients, both dependent on the ionic charge, the dielectric constant and temperature of the solution, and B, also on the interionic distance in the ion pair.

Though Eq. (6.32) has not been tested quantitatively, it nevertheless reflects correctly the character of variation of the diffusion coefficient with concentration and helps to obtain a Δ vs. c curve coinciding in form with the experimental graph.

6.3. THE DIFFUSION POTENTIAL

6.3.1. THE THERMODYNAMIC TREATMENT OF DIFFUSION POTENTIALS

The diffusion potential arises when the ionic mobilities are not equal and there is a concentration gradient. It cannot be regarded as an equilibrium potential, though its value may remain unaltered for a long time under the conditions of steady-state diffusion. Like the diffusion process itself, the diffusion potential is associated with a slight departure from the equilibrium state and thus can be treated thermodynamically.

Consider the most general case when two solutions I and II of different composition and concentration are in contact (Fig. 6.2).

The two solutions are separated by a layer (an interphase region) of transitional composition and concentration. It is in this interphase region that the diffusion potential is localized. Neither the structure of the interphase region, nor the law by which its composition and concentration change are known. It may however be stated that, if we mentally isolate in this region an elementary layer of thickness dx extending from AA to BB and assume that on the left of AA the activities of solution particles are a_1, a_2, a_i and a_k, then on the right of BB the activities will differ from these values by infinitesimal amounts. When one faraday of electricity is transported, irreversibly and isothermally, through the isolated system, its composition will change, and so will its free energy. We will denote this free-energy change by dG and express it in terms of chemical potentials:

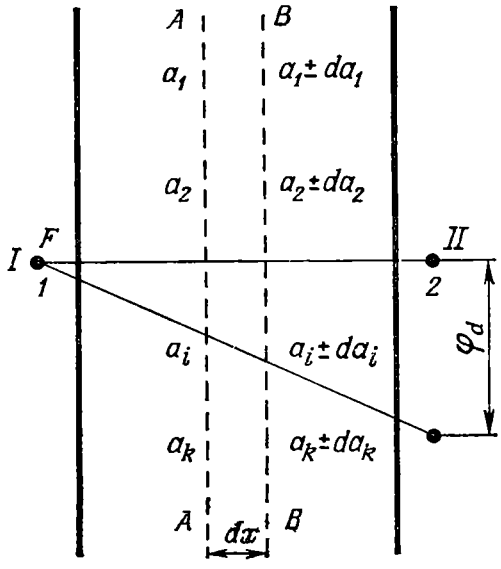


Fig. 6.2. The most general case of two solutions in contact giving rise to a diffusion potential

$$dG = \Sigma m_i \, d\mu_i$$

Since

$$d\mu_i = RT d \ln a_i$$

then

$$dG = RT \, \Sigma m_i d \ln a_i \qquad (6.33)$$

If the fraction of the current carried by a given ionic species is t_i, then the ratio t_i/z_i will be equal to the number of gram-molecules of the transported substance:

$$m_i = \frac{t_i}{z_i}$$

from which and according to Eq. (6.33)

$$dG = RT\Sigma \frac{t_i}{z_i} d \ln a_i \qquad (6.34)$$

At the same time the free-energy change here corresponds to electrical work

$$dG = -Fd\psi_d \qquad (6.35)$$

where ψ_d is the diffusion potential. Replacing dG in Eq. (6.34) by its value from Eq. (6.35) and solving the resulting equation for ψ_d, one can obtain, upon integration, the following general expression for the diffusion potential between the solutions I and II:

$$\psi_d = -\frac{RT}{F} \int_{\text{I}}^{\text{II}} \Sigma \frac{t_i}{z_i} d \ln a_i \qquad (6.36)$$

6.3.2. THE PLANCK AND HENDERSON THEORIES

Equation (6.36) contains individual ionic activities which are not thermodynamically measurable, and any attempt at thermodynamic determination of diffusion potentials is doomed to failure. The values of ψ_d can be calculated if certain assumptions are made as to the structure of the interphase region (diffusion layer), the character of changes in ionic activities and ionic mobilities there, etc. Equation (6.36) was first solved by Planck in 1890, who assumed, firstly, that ionic mobilities are independent of concentration and the properties of the solvent undergo no change upon transition from solution I to solution II and secondly, that the ions diffuse within a strictly limited space on either side of which are solutions I and II whose concentrations remain constant. This occurs when two different solutions move parallel to each other, flowing around both sides of a thin glass diaphragm. It should be noted that since the activity concept was unknown at the time, the Planck theory is applicable to the case when the activities and concentrations are equal ($a_i = c_i$). On the basis of these assumptions one can obtain the following equation for the diffusion potential

$$\psi_d = \frac{RT}{F} \ln \xi \tag{6.37}$$

where ξ is a certain transcendental function; it can be found from the relation

$$\frac{\Sigma \lambda_{+}'' c_i'' \xi - \Sigma \lambda_{+}' c_i'}{\Sigma \lambda_{-}'' c_i'' - \Sigma \lambda_{-}' c_i' \xi} = \frac{\ln \dfrac{\Sigma c_i''}{\Sigma c_i'} - \ln \xi}{\ln \dfrac{\Sigma c_i''}{\Sigma c_i'} + \ln \xi} \cdot \frac{\Sigma c_i'' \xi - \Sigma c_i'}{\Sigma c_i'' - \Sigma c_i' \xi} \tag{6.38}$$

by the iteration method, i.e., by successive choice of such values of ξ which would best equalize the two sides of Eq. (6.38); the single prime refers to solution I and the double prime, to solution II.

Another method for determining ψ_d was proposed by Henderson in 1907. Using the basic assumptions made by Planck, Henderson assumed, in addition, that in the diffusion layer the concentration is changing gradually from solution I to solution II. The concentration of the solution at any point can therefore be expressed as the sum $(1 - x)\,\mathrm{I} + x\mathrm{II}$, where $(1 - x)$ is the fraction of solution I and x the fraction of solution II. The value of x varies from zero to unity in the direction from left to right, from point 1 to point 2. To this model of the interphase region (diffusion layer) there corresponds the following equation for the diffusion potential:

$$\psi_d = -\frac{RT}{F} \cdot \frac{\Sigma \dfrac{\lambda_i}{z_i} (c_i'' - c_i')}{\Sigma \lambda_i (c_i'' - c_i')} \ln \frac{\Sigma \lambda_i c_i'}{\Sigma \lambda_i c_i''} \tag{6.39}$$

Here again the single prime stands for solution I and the double prime for solution II. When substituting the valencies z_i into Eq. (6.39), one should take them with the sign of the particular ion.

Apart from the above two methods for calculating diffusion or liquid junction potentials, other methods were also proposed; the most effective, however, is the method developed by Henderson.

Equations (6.38) and (6.39) are not used, as a rule, because they are cumbersome in their general form. Besides, simple special cases are more important in practice. Two such cases are discussed below.

1. Two solutions of one and the same electrolyte MA but of different concentrations, c' and c''. For this special case the Planck and Henderson equations simplify to

$$\psi_d = \frac{RT}{F} \cdot \frac{\lambda_-^0 - \lambda_+^0}{\lambda_-^0 + \lambda_+^0} \ln \frac{c'}{c''} \tag{6.40}$$

Substituting the activities for the concentrations, one can apply Eq. (6.40) to concentrated solutions. In this case

$$\psi_d = \frac{RT}{F} \cdot \frac{\lambda_- - \lambda_+}{\lambda_- + \lambda_+} \ln \frac{a'}{a''} \tag{6.41}$$

where the ionic mobilities λ_- and λ_+ must correspond to the ionic activities in solutions I and II.

2. Solutions of two dissimilar electrolytes with a common ion (for example, M′A and M″A), the concentrations of the electrolytes being equal, $c' = c''$. For this case the Planck and Henderson equations reduce to the form

$$\psi_d = \frac{RT}{F} \ln \frac{\lambda_+^{0\prime} + \lambda_-^0}{\lambda_+^{0\prime\prime} - \lambda_-^0} \tag{6.42}$$

Taking into account that $\lambda_+^0 + \lambda_-^0 = \lambda_0$, one can write, in place of Eq. (6.42):

$$\psi_d = \frac{RT}{F} \ln \frac{\lambda_0'}{\lambda_0''} \tag{6.43}$$

6.3.3. EXPERIMENTAL DATA ON DIFFUSION POTENTIALS

Some values of diffusion potentials, both experimental and calculated by Eq. (6.43), are given in Table 6.4. The highest diffusion potentials are observed in those cases when one of the solutions used is an acid, because the mobility of the hydrogen ions present in acidic solutions (e.g. in a solution of hydrogen chloride) exceeds the mobilities of all other ions. It can be seen from Table 6.4 that the disparity between the experimental and calculated values of diffusion potential, though not great, reaches several millivolts,

TABLE 6.4

Comparison of Experimental and Calculated Values of Diffusion Potential

Boundary	$c' = c''$	ψ_d, mV	
		experimental	calculated
HCl — KCl	0.1	26.8	28.5
HCl — KCl	0.01	25.7	27.5
HCl — NaCl	0.1	33.1	33.4
HCl — NaCl	0.01	33.1	32.0
HCl — LiCl	0.1	34.9	36.1
HCl — LiCl	0.01	33.8	34.6
NaCl — LiCl	0.01	8.8	7.6
KCl — LiCl	0.01	8.2	7.1

exceeding permissible experimental errors. For this reason it is not recommended to use Eqs. (6.40) and (6.43) or the general equation (6.39) for accurate calculations of diffusion potentials.

Methods have been proposed for diminishing the diffusion potential at the boundary between two different solutions and thereby reducing the error introduced by it into the emf measured. One of these is the salt bridge method. It consists in interposing between two solutions a concentrated solution of an electrolyte with nearly equal cationic and anionic mobilities. In this case one liquid junction is replaced by two; the diffusion potential at each junction (or boundary) is smaller than at the original boundary. Moreover, the diffusion potentials at the two boundaries are often opposed in sign, as a result of which the total diffusion potential is reduced. In such salt bridges use is made of saturated solutions of potassium chloride or ammonium nitrate whose cationic and anionic mobilities are nearly equal (see Table 4.2). Since diffusion potentials cannot be completely eliminated by this method, in measurements requiring high accuracy systems are constructed in which there is no interface (and thus no diffusion potential) between two different solutions.

The absolute value of diffusion potentials (Table 6.4) is small and does not exceed several tens of millivolts. That is why, in industrial electrochemistry diffusion potentials, as a rule, are ignored. True, measures are taken occasionally, for example, in the industrial electrolysis of water, to reduce diffusion potentials in order to cut down power consumption.

There are grounds for believing that diffusion potentials, along with membrane potentials, which are the domain of colloid chemistry, play an important part in the vital activity of animals and plants.

PART THREE

Electrode Equilibrium

CHAPTER 7

Equilibrium Electrode Potentials

7.1. THERMODYNAMIC EXPRESSION FOR EQUILIBRIUM ELECTRODE POTENTIAL

Suppose the following reaction proceeds reversibly and isothermally in an electrochemical system:

$$\nu_A A + \nu_B B + \ldots \overset{\pm zF}{=\!=} \nu_L L + \nu_M M + \ldots \pm \bar{Q}$$

At constant pressure the change of the free energy G in this reaction corresponds to the electrical energy of the system:

$$-\Delta G_{T,\,P} = zFE_{T,\,P}$$

and the reversible emf of the system will be defined as

$$E_{T,\,P} = -\frac{\Delta G_{T,\,P}}{zF} \tag{7.1}$$

At the same time, according to Eq. (I.43),

$$\Delta G = \Sigma \mu_i \nu_i$$

where ν_i is the stoichiometric number for the component possessing the chemical potential μ_i; here, all the values of ν_i are taken as negative for the reactants and as positive for the reaction products. Since, according to Eq. (2.27),

$$\mu_i = \mu_i^0 + RT \ln a_i$$

then, in place of (I.43), one can write

$$\Delta G = \Sigma \mu_i^0 \nu_i + RT \, \Sigma \nu_i \ln a_i$$

or, taking into account the signs before ν_i,

$$\Delta G = \Sigma \mu_i^0 \nu_i + RT \ln \frac{a_L^{\nu_L} a_M^{\nu_M} \ldots}{a_A^{\nu_A} a_B^{\nu_B} \ldots} \tag{7.2}$$

where a positive value is assigned to all the stoichiometric numbers ν_i contained in the logarithmic term. If the activities of all the substances participating in the reaction are equal to unity, i.e., if for any of them $a_i = 1$, or if $a_i \neq 1$ but

$$\frac{a_L^{\nu_L} a_M^{\nu_M} \dots}{a_A^{\nu_A} a_B^{\nu_B} \dots} = 1$$

then

$$\Delta G = \Delta G^0 = \Sigma \mu_i^0 \nu_i = RT \ln K$$

where ΔG^0 = standard change of the free energy
K = equilibrium constant of the chemical reaction in question at definite temperature and pressure.

The quantities ΔG^0 and K have the same meaning here as in the familiar equation of the chemical reaction isotherm

$$\Delta G = RT \ln K + RT \ln \Pi a_i^{\nu_i} \tag{7.3}$$

On the basis of Eqs. (7.1) and (7.2) one can write:

$$E = -\frac{RT}{zF} \ln K - \frac{RT}{zF} \ln \frac{a_L^{\nu_L} a_M^{\nu_M} \dots}{a_A^{\nu_A} a_B^{\nu_B} \dots} \tag{7.4}$$

From Eq. (7.4) it follows that, at $a_i = 1$ for each component and also when the logarithmic expression in the second term on the right-hand side of the equation is equal to unity,

$$E = -\frac{RT}{zF} \ln K \tag{7.5}$$

This value of the emf corresponding to the equilibrium constant of a current-producing electrochemical reaction is denoted by E^0 and is called the *standard emf of an electrochemical system, or cell.* Thus, the emf of any equilibrium electrochemical system is a function of the standard emf and of the activities of the participants of the electrochemical reaction and is given by the equation

$$E = E^0 - \frac{RT}{zF} \ln \frac{a_L^{\nu_L} a_M^{\nu_M} \dots}{a_A^{\nu_A} a_B^{\nu_B} \dots} \tag{7.6}$$

or, in the decimal system,

$$E = E^0 + 2.303 \frac{RT}{zF} \log \frac{a_A^{\nu_A} a_B^{\nu_B} \dots}{a_L^{\nu_L} a_M^{\nu_M} \dots} \tag{7.7}$$

The value of the prelogarithmic factor in Eq. (7.7) as well as in Eq. (7.6) is a linear function of temperature. For any temperature

T it can be found from the formula

$$\frac{0.000198}{z} T \tag{7.8}$$

Some values of the factor $2.303RT/F$ (which will further be denoted as b^0) in Eq. (7.7) are presented in Table 7.1 for temperatures ranging from −50 to +150°C.

TABLE 7.1

Values of the Factor $b^0 = 2.303\ RT/F$ for Different Temperatures [1]

t°C	b^0	t°C	b^0
−50	0.0443	+30	0.0601
±0	0.0542	+40	0.0621
+10	0.0552	+60	0.0661
+20	0.0578	+100	0.0740
+25	0.0592	+150	0.0840

[1] The temperature 25°C is adopted as standard. Most of the values of the various electrochemical quantities have been determined at this temperature.

At room temperature (18-22°C) the value of b^0 may be taken as 0.06 V with sufficient accuracy.

Equations (7.4) and (7.6) lack certainty in the sense that it is not always possible to establish which of the participants of the reaction are the reactants and which the resultants. Therefore, unless some additional conditions are introduced, the emf's may turn out to be of opposite sign for one and the same electrochemical system. Such additional conditions have been worked out and recommended for general use by the International Union of Pure and Applied Chemistry (IUPAC); their significance will become clearer after the concept of "single electrode potential", or "electrode potential", is introduced.

One of the basic features of an electrochemical system is the spatial separation of the participants of the reaction taking place in it. Thus the overall current-producing reaction consists of two partial reactions, each occurring at the respective electrode. Accordingly, the emf of an electrochemical system, which reflects the change of its chemical energy in the course of the overall reaction, must also represent the sum of two electrode potentials. Each of these corresponds to the change of the chemical energy during the respective electrode reaction. Thus

$$E = \varepsilon_1 + \varepsilon_2 \tag{7.9}$$

where ε_1 and ε_2 are the electrode potentials.

Suppose that the following reactions proceed at the first and the second electrode, respectively:

$$\nu_A A + \ldots \overset{\pm zF}{=\!=} \nu_L L \tag{7.10}$$

$$\nu_B B + \ldots \overset{\pm zF}{=\!=} \nu_M M \tag{7.11}$$

Then, in place of Eq. (7.7), one can write

$$E = \varepsilon_1 + \varepsilon_2 = \varepsilon_1^0 + \frac{b^0}{z} \log \frac{a_A^{\nu_A}}{a_L^{\nu_L}} + \varepsilon_2^0 + \frac{b^0}{z} \log \frac{a_B^{\nu_B}}{a_M^{\nu_M}} \tag{7.12}$$

where ε_1^0 and ε_2^0 are standard electrode potentials, their sum being equal to

$$\varepsilon_1^0 + \varepsilon_2^0 = E^0 \tag{7.13}$$

From Eqs. (7.7) and (7.12) it follows that the equation for the electrode potential has the same form as the general thermodynamic equation for the emf of an electrochemical system:

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_A^{\nu_A} \ldots}{a_L^{\nu_L} \ldots} \tag{7.14}$$

with the only difference that it includes the activities of the substances taking part in the respective electrode reaction. The standard electrode potential corresponds to the potential of a reversible electrode when the activity of each of the participants of the electrode reaction is equal to unity, i.e., $a_i = 1$, or when $a_i \neq 1$ but the product of the activities of all the participants is equal to unity.

Experimentally, one can determine only the value of E or E^0, i.e., only the sum of electrode potentials ε_1 and ε_2, or ε_1^0 and ε_2^0, but not the potential of each electrode separately. The quantities ε_1 and ε_2 may be given any values provided that their sum satisfies Eq. (7.9). To eliminate the uncertainty of ε values some additional condition should be introduced.

This additional condition usually consists in selecting a reference electrode, whose potential is taken to be equal to zero, all other electrode potentials being referred to it. In this case electrode potentials are expressed on an arbitrary or relative scale, their values depending on the nature of the adopted reference electrode. Nernst proposed, as the arbitrary zero, the potential of a hydrogen electrode at a unit hydrogen ion concentration and a hydrogen gas pressure of 1 atm. This arbitrary scale is called the *hydrogen scale*. Another idea, suggested by Ostwald, is to use, as the reference potential for the arbitrary scale, the potential of a mercury electrode under conditions in which its charge with respect to the solution is zero. Assuming that in this

case not only the charge but also the potential of the mercury electrode is equal to zero, Ostwald named his scale the *absolute potential scale.* At present the arbitrary hydrogen scale is mainly used, in which the potential of the standard hydrogen electrode (SHE) is chosen as the zero at all temperatures. It differs from the Nernst hydrogen scale in that unit activity and unit fugacity are chosen in place of unit concentration and unit pressure. Thus, electrode potentials can be determined on the hydrogen scale at all temperatures. Their direct comparison is impossible however since the hydrogen electrode potential may vary with temperature, i.e., the arbitrary zero will not be the same at different temperatures.

In certain cases, for example, in polarography, electrode potentials are referred to a normal calomel electrode; they can however be readily converted to hydrogen scale units.

7.2. INTERNATIONAL CONVENTION FOR ELECTROMOTIVE FORCE AND ELECTRODE POTENTIALS

The adoption of the hydrogen scale made it possible to assign definite numerical values to the potentials of the various electrodes and to compare them. It did not however eliminate the uncertainty associated with the use of the equations for electrode potentials (7.7) and (7.14) and with the resolution of the question which substances should be regarded as the reactants and which as the reaction products. This uncertainty once led to a parodoxical situation where America and Europe used opposite signs for electrode potentials (though their absolute values were identical, of course). To unify the sign system for electrode potentials, the IUPAC agreed at Stockholm in 1953 to adopt the European sign convention for general use in all countries of the world. The adoption of the convention for the signs of electrode potentials is associated with the introduction of definite rules for writing the constituents of an electrochemical system, or cell, the overall electrochemical reaction and partial electrode reactions. At present, any electrochemical system is written as follows: (1) the material of one of the two electrodes in the cell; (2) the solution in contact with it; (3) the solution in contact with the other electrode; and (4) the material of the latter electrode. In this notation the electrodes are separated from the adjoining solutions by a single bar, and two different solutions either by a double bar indicating that the diffusion potential (liquid junction potential) has been completely eliminated or by a dashed line if it persists. If an electrode or a solution contains two or several different substances, the latter are separated by a comma (or commas).

For example, the notation

$$\mathrm{Pt,\ H_2/HCl//CuSO_4/Cu} \qquad (7.15)$$

corresponds to an electrochemical system, or cell, consisting of a hydrogen electrode immersed in a solution of hydrochloric acid and a metallic copper plate dipped into a solution of copper sulphate; the diffusion potential at the boundary between the two solutions in this cell has been completely eliminated. The hydrogen electrode is a metal plate (usually, with a sufficiently developed surface) in contact with hydrogen gas and immersed in a solution containing hydrogen ions. Instead of the substances in solutions, one may write only the potential-determining ions. The cell (7.15) may be written thus:

$$\mathrm{Pt,\ H_2/H^+//Cu^{2+}/Cu} \qquad (7.16)$$

since the potential of the electrode on the left depends on the hydrogen ion concentration, and the potential of the right-hand electrode on the concentration of cupric ions.

The electromotive force (emf) of a cell is equal to the potential of the electrode on the right provided that the potential of the electrode on the left is zero. The electrode potential is the emf of a cell with a given electrode on the right and an SHE on the left. The diffusion potential must be eliminated. The emf and the electrode potential are therefore determined by one and the same equation:

$$E = \varepsilon_r - \varepsilon_l = \varepsilon_{\mathrm{H}} \qquad (7.17)$$

in which r stands for the electrode on the right and l for that on the left provided that when determining the electrode potential the left electrode is a standard hydrogen electrode; the subscript H signifies that the electrode potential is expressed on the hydrogen scale. The cell emf is considered positive when the electric current in the electrolysis circuit flows from left to right, and negative when the current flows in the opposite direction. Equation (7.17) defines the emf of a cell as the difference between two electrode potentials each of which is expressed on the same conventional hydrogen scale. Equations (7.9) and (7.17) yield the same result if

$$-\varepsilon_2 = \varepsilon_l$$

and

$$\varepsilon_1 = \varepsilon_r$$

Suppose we are to measure the potential of a zinc electrode using the hydrogen scale. In order to obtain for the zinc electrode the sign of its potential conforming to the International convention, the electrochemical system should be written thus:

$$\mathrm{Pt,\ H_2/H^+//Zn^{2+}/Zn} \qquad (7.18)$$

Since the cell emf is equal in magnitude and identical in sign with the potential of the metallic conductor on the right, the potential of the metallic conductor on the left is taken to be zero. The reaction

proceeding in this cell is written as follows

$$H_2 + Zn^{2+} = 2H^+ + Zn$$

If the electrode on the left is a standard hydrogen electrode, then the cell emf will be equal to the zinc electrode potential. The reaction corresponding to the potential of the zinc electrode must therefore be written as

$$Zn^{2+} + 2e = Zn$$

and the zinc electrode represented as

$$Zn^{2+}/Zn$$

Only when the reaction is written in this way, i.e., when the zinc ions are regarded as reactants, and the metallic zinc as the product of the reaction, will the application of formula (7.14) yield the sign of the zinc electrode potential in accord with the International convention. It is known from experiment that in the cell (7.18) positive electricity flows from right to left and hence the emf as well as the zinc electrode potential equal to it will be a negative quantity [1]. If one writes, in place of (7.18),

$$Zn/Zn^{2+}//H^+/H_2,\ Pt$$

the flow of the current will be reversed, i.e., it will flow from left to right, and the cell emf will be positive; this however is no longer equal to the zinc electrode potential.

The potential of a half-cell corresponds to the definition of the electrode potential if it is written so that the substances in solution are placed on the left, and the electrode material on the right of the bar

$$Zn^{2+}/Zn$$

$$Cl^-/Cl_2,\ Pt$$

$$Fe^{2+},\ Fe^{3+}/Pt$$

The other half-cell placed on the left is here taken to be a standard hydrogen electrode. Reactions giving rise to an electrode potential should be written so that the oxidized forms (reactants) are on the left-hand side of the equation and the reduced forms (resultants) on the right-hand side:

$$Zn^{2+} + 2e = Zn$$

$$\frac{1}{2}Cl_2 + e = Cl^-$$

$$Fe^{3+} + e = Fe^{2+}$$

[1] This implies that measures have been taken to eliminate the diffusion potential (liquid junction potential) and so it is not included in the cell emf.

The recommendations of the Stockholm convention were the subject of discussion at the 17th session of the International Committee of Electrochemical Thermodynamics and Kinetics (CITCE, Japan, 1966). The nomenclature panel of the Committee suggested that the use of the terms "electromotive force" and "potential" should be limited and the term "voltage" used on a wider scale retaining the word "potential" only in such combinations as "electrical (electrostatic) potential" and "chemical potential". It was recommended to replace the term "electrode potential" by "electrode voltage" and to use the concept of "electromotive force", which is equivalent to "chemical potential of an electrochemical cell, or system", only in connection with free energy change occurring in the course of a reversible electrochemical reaction, and to define it with the aid of the equation

$$E = -\frac{\Delta G}{zF}$$

As to the quantity measured experimentally it was recommended to use the term "the voltage of a system (cell)" or "the electrical voltage of a system (cell)" and to designate it by the letter U. The quantity U is defined as the difference between the inner potentials (see page 211) of two identical conductors connected to the electrodes of an electrochemical cell. The cell notation is the reversed notation used for defining the emf. For example, the cell (7.18) is constituted thus:

$$Cu'/Zn/Zn^{2+}//H^{+}/H_2,\ Pt/Cu$$

and the voltage across the cell is measured as the difference between the inner potentials in the conductors Cu′ and Cu. If the cell is in electrochemical equilibrium, then from the definition of the emf and voltage it follows that

$$E + U_r = 0$$

where U_r is the reversible voltage across the cell. Naturally

$$U_r = -E = \frac{\Delta G}{zF}$$

Similar definitions are proposed for the electrode voltage. When a current I is passed through a cell, the voltage must always be equal to U, but the emf ($E = -U_r$) is pegged specifically to the equilibrium state and is not a function of current intensity.

The suggestions made by the Nomenclature Commission have not yet gained universal recognition and therefore further in this book electrode equilibrium will be treated in accord with the Stockholm convention.

7.3. CLASSIFICATION OF ELECTRODES

As follows from Eq. (7.14)

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_A^{\nu_A} \dots}{a_L^{\nu_L} \dots}$$

the potential of any electrode at a given temperature and pressure is determined by the magnitude of the standard potential ε^0 and the activities of the substances taking part in the electrode reaction. The standard potential is a constant which is specific for each electrode, while the activities of the reacting species may be different, depending on the concentration of the reaction medium. The effect of the activities of the species involved on the electrode potential is directly associated with the nature of the electrode reaction, and this relationship lies at the basis of the classification of electrodes. It is customary to distinguish electrodes of the first or second kind, gas, redox, and some special types of electrodes.

7.3.1. ELECTRODES OF THE FIRST KIND

Metal electrodes of the first kind can be represented schematically as

$$M^{z+}/M$$

and non-metal ones (metalloids) as

$$Me^{z-}/Me$$

The electrode reaction is written accordingly

$$M^{z+} + ze = M$$

or

$$Me + ze = Me^{z-}$$

Substituting the activities of the species involved in the electrode reaction into the general equation of electrode potential (7.14) yields:

$$\varepsilon_{M^{z+}/M} = \varepsilon^0_{M^{z+}/M} + \frac{RT}{zF} \ln \frac{a_{M^{z+}}}{a_M} \tag{7.19}$$

for a metal electrode of the first kind and

$$\varepsilon_{Me^{z-}/Me} = \varepsilon^0_{Me^{z-}/Me} + \frac{RT}{zF} \ln \frac{a_{Me}}{a_{Me^{z-}}} \tag{7.20}$$

for a non-metal electrode of the first kind. Considering that the activity of a pure solid at a given temperature is constant and assuming it to be equal to unity, expressions (7.19) and (7.20) can be simpli-

fied to

$$\varepsilon_{M^{z+}/M} = \varepsilon^0_{M^{z+}/M} + \frac{b^0}{z} \log a_{M^{z+}} \tag{7.21}$$

and

$$\varepsilon_{Me^{z-}/Me} = \varepsilon^0_{Me^{z-}/Me} - \frac{b^0}{z} \log a_{Me^{z-}} \tag{7.22}$$

It can be seen from Eqs. (7.21) and (7.22) that the potential of an electrode of the first kind depends on the activity of only one ionic species. The ions that govern the magnitude of electrode potential are called *potential-determining ions.* In the case of metal electrodes of the first kind the cations of the metal, and with non-metal electrodes the anions of the non-metal play the part of potential-determining ions. A silver plate immersed in a solution of silver nitrate, or a copper plate dipped in a solution of copper sulphate are typical examples of metal electrodes of the first kind. A silver electrode of the first kind is represented as

$$Ag^+/Ag$$

with the electrode reaction

$$Ag^+ + e = Ag$$

and the electrode potential

$$\varepsilon_{Ag^+/Ag} = \varepsilon^0_{Ag^+/Ag} + b^0 \log a_{Ag^+} \tag{7.23}$$

After substituting the numerical values of ε^0 and b^0 at 25°C one has

$$\varepsilon_{Ag^+/Ag} = +0.799 + 0.0592 \log a_{Ag^+} \tag{7.24}$$

For a copper electrode of the first kind we have, accordingly,

$$Cu^{2+}/Cu$$

$$Cu^{2+} + 2e = Cu$$

and

$$\varepsilon_{Cu^{2+}/Cu} = \varepsilon^0_{Cu^{2+}/Cu} + \frac{b^0}{2} \log a_{Cu^{2+}} \tag{7.25}$$

or, at 25°C,

$$\varepsilon_{Cu^{2+}/Cu} = +0.34 + 0.03 \log a_{Cu^{2+}} \tag{7.26}$$

A selenium electrode may be quoted as an example of a non-metal electrode of the first kind:

$$Se^{2-}/Se$$

$$Se + 2e = Se^{2-}$$

$$\varepsilon_{Se^{2-}/Se} = \varepsilon^0_{Se^{2-}/Se} - \frac{b^0}{2} \log a_{Se^{2-}} \tag{7.27}$$

or, at 25°C,

$$\varepsilon_{Se^{2-}/Se} = -0.92 - 0.03 \log a_{Se^{2-}}$$

Metal electrodes of the first kind are of greater practical importance and are easier to construct than non-metal electrodes. In the latter case measurements of the potential usually require insertion of an inert metal conductor into the system consisting of a non-metal and its ions.

7.3.2. ELECTRODES OF THE SECOND KIND

Electrodes of the second kind are half-cells consisting of a metal covered by one of its sparingly soluble compounds (salt, oxide, or hydroxide), immersed in a solution having the same anion as the sparingly soluble compound of the electrode metal. A generalized electrode of the second kind may be expressed as

$$A^{z-}/MA,\ M$$

with the electrode reaction

$$MA + ze = M + A^{z-}$$

The equation for the electrode potential will then be

$$\varepsilon_{A^{z-}/MA,\,M} = \varepsilon^0_{A^{z-}/MA,\,M} + \frac{b0}{z} \log \frac{a_{MA}}{a_{A^{z-}} a_M} \qquad (7.28)$$

Since the activities of metal M and solid substance MA are constant, the equation for the potential of the electrode of the second kind may be simplified to

$$\varepsilon_{A^{z-}/MA,\,M} = \varepsilon^0_{A^{z-}/MA,\,M} - \frac{b0}{z} \log a_{A^{z-}} \qquad (7.29)$$

Thus, the potential of an electrode of the second kind depends on the anionic activity of the sparingly soluble compound of the electrode metal. The values of the potentials of electrodes of the second kind are readily reproducible and stable. These electrodes are often employed as standard half-cells or reference electrodes[1] with respect to which the potentials of other electrodes are measured. Of greatest interest in practice are calomel, mercury-mercurous sulphate, silver-silver chloride, mercury-mercuric oxide, and antimony electrodes.

Calomel Electrodes. The calomel electrode consists of a pool of mercury covered with a paste of mercury and calomel and immersed in a solution of potassium chloride acting as electrolyte:

$$Cl^-/Hg_2Cl_2,\ Hg$$

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[1] They are often called *subsidiary* or *secondary reference electrodes* in distinction to the hydrogen electrode, which is known as the *primary reference electrode.*—*Tr.*

The electrode reaction is the reduction of the calomel (mercurous chloride) to metallic mercury and a chloride anion:

$$Hg_2Cl_2 + 2e = Hg + 2Cl^- \qquad (7.30)$$

The potential of the calomel electrode is reversible with respect to chloride ions:

$$\varepsilon_{Cl^-/Hg_2Cl_2,\,Hg} = \varepsilon^0_{Cl^-/Hg_2Cl_2,\,Hg} - b^0 \log a_{Cl^-} \qquad (7.31)$$

and is governed by their activity. The potential of the calomel electrode at 250°C is found from the equation

$$\varepsilon_{Cl^-/Hg_2Cl_2,\,Hg} = +0.2678 - 0.0592 \log a_{Cl^-} \qquad (7.32)$$

The most frequently used electrodes are calomel electrodes in which the concentration of potassium chloride is either at saturation or equal to 1.0 or 0.1 g-eq/litre. The potentials of calomel electrodes on the hydrogen scale are calculated with the aid of the following equations which hold for temperatures ranging from 0 to 100°C:

(1) for a 0.1*N* calomel electrode

$$\varepsilon_{0.1} = 0.3337 - 8.75 \times 10^{-5} (t - 25) - 3 \times 10^{-6} (t - 25)^2$$

(2) for a 1.0*N* calomel electrode

$$\varepsilon_{1.0} = 0.2801 - 2.75 \times 10^{-4} (t - 25) - 2.5 \times 10^{-6} (t - 25)^2 - 4 \times 10^{-9} (t - 25)^3$$

(3) for a saturated calomel electrode

$$\varepsilon_{sat} = 0.2412 - 6.61 \times 10^{-4} (t - 25) - 1.75 \times 10^{-6} (t - 25)^2 - 9.0 \times 10^{-10} (t - 25)^3$$

Calomel electrodes, especially saturated ones, are convenient in use because the diffusion potential arising in a cell at the junction between the saturated potassium chloride solution and the solution under study is insignificant; it may be ignored in many cases where high accuracy is not required.

Mercury-Mercurous Sulphate and Silver-Silver Chloride Electrodes. Mercury-mercurous sulphate electrodes SO_4^{2-}/Hg_2SO_4, Hg are similar to calomel electrodes with the difference that the mercury pool is covered with a paste of mercury and mercurous sulphate, and sulphuric acid is used as the solution. The activity dependence of the potential of a mercury-mercurous sulphate electrode at 25°C is described by the equation

$$\varepsilon_{SO_4^{2-}/Hg_2SO_4,\,Hg} = 0.6156 - 0.0296 \log a_{SO_4^{2-}} \qquad (7.33)$$

The silver-silver chloride electrode is a system represented by

$$Cl^-/AgCl,\ Ag$$

and its potential is given by the equation

$$\varepsilon_{Cl^-/AgCl,\,Ag} = \varepsilon^0_{Cl^-/AgCl,\,Ag} - b^0 \log a_{Cl^-} \tag{7.34}$$

or, at 25°C,

$$\varepsilon_{Cl^-/AgCl,\,Ag} = 0.2224 - 0.0592 \log a_{Cl^-} \tag{7.35}$$

Mercury-mercurous sulphate and silver-silver chloride electrodes should be used where the half-cell under study contains, as the electrolyte, sulphuric acid (or sulphates) or hydrochloric acid (or chlorides). In order to reduce the diffusion potential (liquid junction potential), the concentrations of these electrolytes in reference (or comparison) electrodes should be the same as in the half-cell being tested, or close to it. The temperature coefficients of the potentials of mercury-mercurous sulphate, silver-silver chloride and calomel electrodes are dependent on the solution composition. Since, in contrast to calomel electrodes, in the first two types of electrode use is made of solutions of very different concentrations, the values of their temperature coefficients will not be given here.

Though the potentials of the electrodes of the second kind described above are governed by the activity of the corresponding anions, one can nevertheless write equations for them coinciding in form with the equations for the potentials of electrodes of the first kind. For example, according to the solubility product principle, the product of the activities of the silver ions and the chloride ions in solution will be equal to the solubility product of silver chloride, K_{AgCl}:

$$a_{Ag^+} \times a_{Cl^-} = K_{AgCl}$$

$$a_{Cl^-} = \frac{K_{AgCl}}{a_{Ag^+}} \tag{7.36}$$

Substituting the value of a_{Cl^-} from Eq. (7.36) into Eq. (7.34) gives

$$\varepsilon_{Cl^-/AgCl,\,Ag} = \varepsilon^0_{Cl^-/AgCl,\,Ag} - b^0 \log K_{AgCl} + b^0 \log a_{Ag^+} \tag{7.37}$$

Comparing Eqs. (7.23) and (7.37), one obtains the following equality

$$\varepsilon^0_{Cl^-/AgCl,\,Ag} - b^0 \log K_{AgCl} = \varepsilon^0_{Ag^+/Ag} \tag{7.38}$$

The solubility product of sparingly soluble salts can be found by comparing the potentials of the corresponding electrodes of the first and the second kind. Equation (7.37), in which the potential of an electrode of the second kind is represented as a function of the activity of metal ions, is less convenient in practice than Eq. (7.34) since the activities of metal ions are negligibly small and are derived from the activities of the corresponding anions.

Metal-Metal Oxide Electrodes. This group of reference electrodes are particularly interesting since the role of the anions of the sparingly soluble compound of the electrode metal is played by hydroxyl ions. Examples are provided by the following electrode systems:

(1) the mercury-mercuric oxide electrode

$$OH^-/HgO,\ Hg$$

(2) the antimony electrode

$$OH^-/Sb_2O_3,\ Sb$$

The equations for the electrode reactions and potentials of these electrodes are, respectively,

$$HgO + H_2O + 2e = Hg + 2OH^-$$

$$Sb_2O_3 + 3H_2O + 6e = 2Sb + 6OH^-$$

and

$$\varepsilon_{OH^-/HgO,\ Hg} = \varepsilon^0_{OH^-/HgO,\ Hg} - b^0 \log a_{OH^-} \qquad (7.39)$$

$$\varepsilon_{OH^-/Sb_2O_3,\ Sb} = \varepsilon^0_{OH^-/Sb_2O_3,Sb} - b^0 \log a_{OH^-} \qquad (7.40)$$

Equations (7.39) and (7.40) are obtained from the general equation for the electrode potential (7.14) under the assumption that not only the activities of the corresponding metals and their oxides are constant, but so is the activity of the water, which also takes part in the electrode reaction. This assumption practically does not affect the accuracy of the equations for the electrode potential and is widely used where the concentration of the solution is not very great.

Like metal-metal salt electrodes of the second kind, metal-metal oxide electrodes of the second kind can be reduced to the corresponding electrodes of the first kind. Therefore they are reversible not only with respect to hydroxyl ions but to the ions of a metal as well. Besides, they are also reversible with respect to hydrogen ions because the ionic product of water

$$K_W = a_{H^+} \times a_{OH^-}$$

at a given temperature is constant for any aqueous electrolytic solution. Substitution of the value of a_{OH^-} from the last equation into Eq. (7.39) or (7.40) gives, respectively,

$$\varepsilon_{OH^-/HgO,\ Hg} = \varepsilon^0_{OH^-/HgO,\ Hg} - b^0 \log K_W + b^0 \log a_{H^+} = \varepsilon^0_{H^+/HgO,\ Hg} - b^0\ pH \qquad (7.41)$$

and

$$\varepsilon_{OH^-/Sb_2O_3,\ Sb} = \varepsilon^0_{OH^-/Sb_2O_3,\ Sb} - b^0 \log K_W + b^0 \log a_{H^+} = \varepsilon^0_{H^+/Sb_2O_3,Sb} - b^0\ pH \qquad (7.42)$$

After substitution of numerical values of the constant terms into Eqs. (7.41) and (7.42) they assume the following form for 25°C

$$\varepsilon_{OH^-/HgO,\ Hg} = 0.92 - 0.06\ pH \qquad (7.43)$$

$$\varepsilon_{OH^-/Sb_2O_3,\ Sb} = 0.145 - 0.06\ pH \qquad (7.44)$$

Metal-metal oxide electrodes can be used as reference electrodes for any acid or alkali solution since hydrogen or hydroxyl ions are

potential-determining ions in this case. The mercury-mercuric oxide electrode is recommended only for solutions with pH > 7 because mercury oxides are perceptibly soluble in acids. The antimony electrode cannot be employed as a reference electrode because of the instability of its surface oxide (oxides other than Sb_2O_3 may form). It finds application as an indicator electrode for approximate pH measurements in moderately acidic and neutral solutions.

7.3.3. GAS ELECTRODES

General Description of Gas Electrodes. A gas electrode is a half-cell consisting of a metallic conductor in simultaneous contact with the corresponding gas and the solution containing its ions. A gas electrode cannot be designed or the potential of the system composed of a gas and a solution of its ions measured without the provision of a metallic conductor just as any other electrode is inconceivable without an electronic conductor.

Besides, a metal in gas electrodes not only creates an electrical contact between the gas and the solution containing its ions, but also accelerates the attainment of electrode equilibrium, i.e., serves as catalyst for the electrode reaction. Hence, only those metals can be used in gas electrodes which possess high catalytic activity with respect to the reaction between the gas and its ions in solution. Further, the potential of the metal in a gas electrode must be independent of the activity of other ions present in the solution, in particular of its own metal ions. Functioning as catalyst for the reaction between the gas and its ions in solution, the metal must at the same time be inert with respect to other reactions which may occur in the system. Finally, the metal must provide as large an interface as possible on which the reversible reaction converting the gas to the ionic state could proceed. All these requirements are best met by platinum, which is most frequently used. To produce a large surface area the platinum is coated electrolytically with finely divided platinum black, this resulting in so-called platinized platinum, Pt, Pt. Gas electrodes are very sensitive to any change in the condition of the platinized surface, in particular, to catalytic poisons. To obtain reproducible values of the potential corresponding to the true equilibrium conditions of functioning of gas electrodes, it is necessary to observe various precautionary measures, which may involve considerable difficulties.

The Hydrogen Electrode. The gaseous hydrogen electrode may be represented as

$$H^+/H_2,\ Pt$$

The corresponding electrode reaction is

$$2H^+ + 2e = H_2$$

from which and from Eq. (7.14)

$$\varepsilon_{H^+/H_2} = \varepsilon^0_{H^+/H_2} + 2.303 \frac{RT}{2F} \log \frac{a^2_{H^+}}{P_{H_2}} \tag{7.45}$$

or

$$\varepsilon_{H^+/H_2} = \varepsilon^0_{H^+/H_2} + b^0 \log a_{H^+} - \frac{b^0}{2} \log P_{H_2} \tag{7.46}$$

It is seen from expressions (7.45) and (7.46) that the hydrogen electrode potential depends not only on the hydrogen ion activity but also on the partial hydrogen gas pressure. Hence, the hydrogen electrode (as well as other gas electrodes) is more complicated than electrodes of the first or second kind, the potentials of which are directly dependent on the activity of a single ionic species. The standard hydrogen electrode potential ε^0_{H+/H_2} is conventionally taken as zero at all temperatures and therefore one can write, in place of (7.45):

$$\varepsilon_{H^+/H_2} = 2.303 \frac{RT}{2F} \log \frac{a^2_{H^+}}{P_{H_2}} \tag{7.47}$$

For a partial hydrogen pressure of one atmosphere Eq. (7.47) simplifies to

$$\varepsilon_{H+/H_2} = b^0 \log a_{H+} \tag{7.48}$$

or

$$\varepsilon_{H+/H_2} = - b^0 \text{ pH} \tag{7.49}$$

Thus, under definite conditions the hydrogen electrode potential is a direct expression of the pH value.

The Oxygen Electrode. The oxygen gas electrode is symbolized by

$$OH^-/O_2, \text{ Pt}$$

The reaction occurring at the oxygen electrode may be written as follows:

$$O_2 + 2H_2O + 4e = 4OH^- \tag{7.50}$$

On this basis and from Eq. (7.14) one obtains the following expression for the reversible oxygen gas electrode potential:

$$\varepsilon_{OH^-/O_2} = \varepsilon^0_{OH^-/O_2} + 2.303 \frac{RT}{4F} \log \frac{P_{O_2}}{a^4_{OH^-}} \tag{7.51}$$

or

$$\varepsilon_{OH^-/O_2} = \varepsilon^0_{OH^-/O_2} + \frac{b^0}{4} \log P_{O_2} - b^0 \log a_{OH^-} \tag{7.52}$$

the activity of the water being included in the value of ε^0. At 25°C the theoretical value of the standard potential of the oxygen electro-

de obtained from thermodynamic data is +0.401 V. Therefore, at $P_{O_2} = 1$ atm and 25°C the expression for the equilibrium oxygen electrode can be written as

$$\varepsilon_{OH^-/O_2} = 0.401 - 0.0592 \log a_{OH^-} \qquad (7.53)$$

In practice, however, it is rather difficult to set up an oxygen electrode whose behaviour would be described by the derived equations. This is explained by the specific features of gas electrodes in general and, in addition, by the tendency of oxygen to oxidize metals, especially in a moist atmosphere. For this reason, on the principal electrode reaction is imposed a reaction corresponding to a metal-metal oxide electrode of the second kind. Oxide films may form even on platinum and then the behaviour of the oxygen electrode will not conform to theoretical equations. These deviations manifest themselves, for example, in the way the potential varies with oxygen pressure. Moreover, there are grounds for believing that, apart from the formation of surface oxides, the reaction taking place at the oxygen electrode differs from the reaction forming the basis for the equation of the oxygen electrode potential. According to the data obtained by Berl (1943) and confirmed by other workers, part of the oxygen is reduced at the electrode to hydrogen peroxide ions rather than to water:

$$O_2 + H_2O + 2e = HO_2^- + OH^-$$

The potential of such an oxygen electrode is given by the equation

$$\varepsilon_{HO_2^-,\,OH^-/O_2} = \varepsilon^0_{HO_2^-,\,OH^-/O_2} + \frac{b^0}{2} \log \frac{P_{O_2}}{a_{HO_2^-} a_{OH^-}} \qquad (7.54)$$

which differs from Eq. (7.50) in the magnitude of the standard potential (here ε^0 at 25°C is 0.076 V) and the manner in which the electrode potential depends on the hydroxyl ion activity. This is why the experimentally measured values of the oxygen electrode potential usually do not coincide with theory.

The Chlorine Electrode. The setting up of the reversible chlorine gas electrode

$$Cl^-/Cl_2,\ Pt$$

entails considerable difficulties. Theoretically, the relevant electrode reaction is simple:

$$Cl_2 + 2e = 2Cl^-$$

and the electrode potential can be expressed by

$$\varepsilon_{Cl^-/Cl_2} = \varepsilon^0_{Cl^-/Cl_2} + 2.303 \frac{RT}{2F} \log \frac{P_{Cl_2}}{a^2_{Cl^-}} \qquad (7.55)$$

It should however be kept in mind that on the basic electrode process are imposed secondary reactions in which chlorine takes part and

which result in the formation of products of chlorine hydrolysis—hypochlorites. The high positive value of the standard potential of the chlorine electrode (+1.358 V at 25°C) complicates the choice of a sufficiently stable electrode material inert with respect to chlorine. This is also one of the causes for the deviation of the experimental values of the chlorine electrode potential from its reversible value determined on the basis of thermochemical data. Notwithstanding this, a number of authors have succeeded in obtaining an experimental value of the chlorine electrode potential coinciding with the theoretical value.

The study of the behaviour of gas electrodes has been attracting much attention lately in connection with intensified work on so-called fuel cells.

7.3.4. AMALGAM ELECTRODES

The amalgam electrode is a half-cell in which an amalgam of some metal is in contact with a solution containing ions of this metal. A generalized amalgam electrode may be represented by

$$M^{z+}/M_m,\ Hg$$

It is assumed here that the amalgam electrode potential is controlled by the reaction

$$mM^{z+} + zme = M_m\ (Hg)$$

which means that mercury behaves as an inert medium in which metal M is dissolved and the ions of this metal play the role of potential-determining ions. The potential of the amalgam electrode is given by

$$\varepsilon_{M^{z+}/M_m,\,Hg} = \varepsilon^0_{M^{z+}/M_m,\,Hg} + 2.303\frac{RT}{zmF}\log\frac{a^m_{M^{z+}}}{a_{M_m(Hg)}} \qquad (7.56)$$

It depends not only on the activity of the metal ions in solution but also on their activity in the amalgam. If the metal is dissolved in mercury as individual atoms ($m = 1$), then the previous equation is replaced by

$$\varepsilon_{M^{z+}/M,\,Hg} = \varepsilon^0_{M^{z+}/M,\,Hg} + \frac{b^0}{z}\log\frac{a_{M^{z+}}}{a_{M(Hg)}} \qquad (7.57)$$

It should be borne in mind that mercury is capable of reacting with a metal with the formation of intermetallic compounds soluble in mercury:

$$xM^{z+} + xze + yHg = M_xHg_y\ (Hg)$$

The magnitude of the electrode potential will here be a function of the composition of the resulting compounds:

$$\varepsilon_{M^{2+}/M_xHg_y,\,Hg} = \varepsilon^0_{M^{2+}/M_xHg_y,\,Hg} + 2.303\frac{RT}{xzF}\log\frac{a^x_{M^{2+}}}{a_{M_xHg_y(Hg)}} \qquad (7.58)$$

Amalgam electrodes find wide application in industry and in laboratory work. An example is provided by the cadmium amalgam electrode

$$Cd^{2+}/Cd,\ Hg$$

on which the following reaction takes place

$$Cd^{2+} + 2e = Cd\ (Hg)$$

Its potential is determined by the formula

$$\varepsilon_{Cd^{2+}/Cd,\ Hg} = \varepsilon^0_{Cd^{2+}/Cd,\ Hg} + \frac{b^0}{2} \log \frac{a_{Cd^{2+}}}{a_{Cd(Hg)}} \qquad (7.59)$$

Electrodes of this type containing 12.5 per cent cadmium are used to prepare standard, or normal Weston cells, the electromotive force of which practically does not vary with time. Amalgams most widely used in industry are made of alkali metals obtained as intermediates in the production of chlorine and alkalis.

7.3.5. OXIDATION-REDUCTION OR REDOX ELECTRODES

Any electrode reaction involves a change in the oxidized or reduced state of the substances participating in the reaction; in this sense all electrodes may be regarded as oxidation-reduction systems. But the term *oxidation-reduction electrodes*, or briefly *redox electrodes*, is usually confined to those cases where metals or gases take no direct part in the electrode reaction. In a redox electrode, the metal, which supplies or accepts electrons, acquires a potential corresponding to a steady redox equilibrium. The metallic conductor here must meet the same requirements as in gas electrodes. A distinction should be made between *simple* and *multiple redox electrodes*. With simple electrodes the reaction consists in changing the valency of the ions, their composition remaining constant. Examples are provided by the following electrode processes:

$$Fe^{3+} + e = Fe^{2+}$$

$$Tl^{3+} + 2e = Tl^{+}$$

$$MnO_4^- + e = MnO_4^{2-}$$

$$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$$

If the oxidized ions are designated as Ox and the reduced ions as Red, then all the above reactions can be represented by a single general equation:

$$Ox + ze = Red \qquad (7.60)$$

A simple generalized redox electrode is written as

$$\text{Red, Ox/Pt}$$

and its potential is given by the equation

$$\varepsilon_{\text{Red, Ox}} = \varepsilon^0_{\text{Red, Ox}} + 2.303 \frac{RT}{zF} \log \frac{a_{\text{Ox}}}{a_{\text{Red}}} \qquad (7.61)$$

Equation (7.61) shows that the potential of a simple redox electrode is determined by the activity ratio of ions in two different states of oxidation. If a cell yields ions of several valencies, there will be as many redox electrodes as the number of pairs that can be set up. For example, if a cell can exist as ions of three different valencies, then there will be three different redox electrodes.

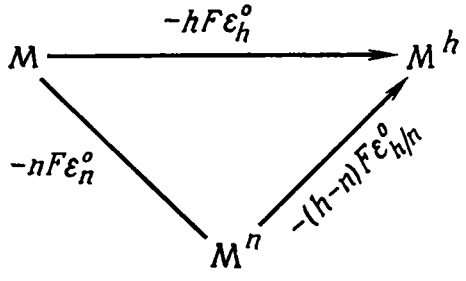
The potentials of simple redox electrodes can be easily related to the potentials of the corresponding electrodes of the first kind. Suppose, for example, that metal M is capable of existing in solution in the form of ions of high valency M^h and low valency M^n. In this case two electrodes of the first kind

$$M^h/M \text{ and } M^n/M$$

and one redox electrode

$$M^n,\ M^h/M$$

can be constituted. The potentials of these electrodes are, respectively, $\varepsilon^0_{M^h/M}$, $\varepsilon^0_{M^n/M}$, and $\varepsilon^0_{M^n,\ M^h/M}$. The relation between these quantities can be found by visualizing the process of electrochemical dissolution of metal M with high-valency ions M^h being produced either directly or through the intermediate formation of low-valency ions M^n. It is supposed that the process of dissolution occurs reversibly and isothermally in an infinitely large volume of solution in which the activity of each ionic species is unity. This process may be represented by the following simple cycle:



From this cycle it follows that

$$h\varepsilon^0_h = n\varepsilon^0_n + (h - n)\,\varepsilon^0_{n,h} \qquad (7.62)$$

Using Eq. (7.62) known as Luther's rule, one can calculate the standard potential of any one of the three electrodes if the values for the other two electrodes are known. Equation (7.62) is used in

cases where the direct determination of one of the potentials is either very difficult or impossible. For instance, the potential of the electrode of the first kind Fe^{3+}/Fe, which is not directly measurable because of the instability of ferric ions under these conditions, can be found from the experimentally accessible standard potentials of an electrode of the first kind Fe^{2+}/Fe and a simple redox electrode Fe^{2+}, Fe^{3+}/Pt:

$$\varepsilon^0_{Fe^{3+}/Fe} = \frac{2}{3}\varepsilon^0_{Fe^{2+}/Fe} + \frac{1}{3}\varepsilon^0_{Fe^{2+},\,Fe^{3+}}$$

In the case of multiple redox electrodes the reaction involves a change in the valencies of the reacting particles and in their composition. Reactions of this type usually involve hydrogen ions and water molecules; the participation of water molecules however does not affect the equations for the electrode potential because the activity of the water remains constant throughout the reaction, except in very concentrated solutions. Using the previous notation (Ox for oxidized forms and Red for reduced forms), multiple redox electrode can be represented as

$$\text{Red, Ox, } H^+/Pt$$

Its potential must be a function not only of the activities of the oxidized and reduced particles but of the hydrogen ion activity as well. The dependence on the latter is determined by the nature of the reacting particles. For example, for the system permanganate-bivalent manganese ions in which the following reaction takes place

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$

the electrode potential is given by the equation

$$\varepsilon_{Mn^{2+},\,MnO_4^-} = \varepsilon^0_{Mn^{2+},\,MnO_4^-} + 2.303\frac{RT}{5F}\log\frac{a_{MnO_4^-}a^8_{H^+}}{a_{Mn^{2+}}} \qquad (7.63)$$

or

$$\varepsilon_{Mn^{2+},\,MnO_4^-} = \varepsilon^0_{Mn^{2+},\,MnO_4^-} + \frac{b^0}{5}\log\frac{a_{MnO_4^-}}{a_{Mn^{2+}}} + \frac{8}{5}b^0\log a_{H^+} \qquad (7.64)$$

For the quinone-hydroquinone system with the reaction

$$C_6H_4O_2 + 2H^+ + 2e = C_6H_4(OH)_2$$

the electrode potential is given by

$$\varepsilon_{Q,\,HQ} = \varepsilon^0_{Q,\,HQ} + 2.303\frac{RT}{2F}\log\frac{a_Q a^2_{H^+}}{a_{HQ}} \qquad (7.65)$$

or

$$\varepsilon_{Q,\,HQ} = \varepsilon^0_{Q,\,HQ} + \frac{b^0}{2}\log\frac{a_Q}{a_{HQ}} + b^0\log a_{H^+} \qquad (7.66)$$

where the subscripts Q and HQ stand, respectively, for quinone and hydroquinone.

An investigation into the dependence of the potential of multiple redox electrodes on the pH of the solution can therefore yield information on the nature of a particular redox reaction. And, conversely, multiple redox electrodes can be used as indicator electrodes in pH measurements. Electrodes reversible with respect to the quinone-hydroquinone system are widely used for this purpose. An equimolecular mixture of quinone and hydroquinone is introduced into a solution whose pH value is to be measured. Assuming that the ratio of the concentrations of quinone and hydroquinone is equal to that of their activities

$$\frac{c_Q}{c_{HQ}} = \frac{a_Q}{a_{HQ}} = 1$$

we can simplify Eq. (7.62) to

$$\varepsilon_{Q,\,HQ} = \varepsilon^0_{Q,\,HQ} + b^0 \log a_{H^+} = \varepsilon^0_{Q,\,HQ} - b^0\,pH$$

The potential of such an electrode, known as a quinhydrone electrode, will be directly determined by the pH of the electrolyte.

When the reactants in a redox reaction are complex organic substances, say, proteins, the metallic conductor in contact with them loses its ability to assume an equilibrium potential value corresponding to this system. In such cases so-called potential mediators are used in measuring the redox potential. These mediators represent a simple redox system, often of the type Ce^{3+}, Ce^{4+}. When cerium salts of concentration many times lower than that of the substances forming a multiple redox system are added to the reaction medium, the following reaction will take place:

$$Ox + Ce^{3+} = Red + Ce^{4+}$$

and the simple redox system, having reached an equilibrium with the multiple system, assumes its potential. The metallic conductor acquires the steady potential of the mediator and the identical potential of the multiple redox system. The change of the original potential as a result of the reaction between the principal redox substances and the mediator may be ignored since the concentration of the latter is negligibly small compared with those of the substances constituting the complex redox system. The concentrations of these substances therefore remain practically constant.

7.3.6. THE GLASS ELECTRODE

The glass electrode differs from the electrodes discussed above in that no electrons take part in the corresponding electrode reaction. The electrode reaction here is merely an exchange of hydrogen

ions between two phases—solution and glass:

$$H^+ = H_G^+$$

The charge of the hydrogen ion corresponds to the elementary positive quantity of electricity, and the transfer of the hydrogen ion from one phase to the other is equivalent to the transport of unit charge, i.e., the value of z in the equation for the glass electrode potential should be taken as unity:

$$\varepsilon_G = \varepsilon_G^0 + 2.303 \frac{RT}{F} \log \frac{a'_{H^+}}{a_{H_G^+}} \tag{7.67}$$

But in fact the alkali metal ions contained in the glass are also drawn into the exchange reaction. Part of these ions are replaced by hydrogen ions and pass into solution:

$$H^+ + M_G^+ = H_G^+ + M^+$$

where M^+ may be ions of lithium, sodium or some other alkali metal, depending on the type of glass used. To this general equation there corresponds the following exchange constant

$$K_e = \frac{a_{H^+} a_{M_G^+}}{a_{H_G^+} a_{M^+}} \tag{7.68}$$

The value of this constant depends on the properties of the glass and on temperature; for ordinary glass electrodes at room temperature it ranges from 10^{-10} to 10^{-14}. Assuming that in the type of glass used the sum of the activities of hydrogen ions and alkali metal ions is constant, i.e.,

$$a_{H_G^+} + a_{M_G} = a$$

we can rewrite the expression for the exchange constant as follows

$$K_e = \frac{a_{H^+}(a - a_{H_G^+})}{a_{H_G^+} a_{M^+}} \tag{7.69}$$

Solving this equation for $a_{H^+}/a_{H_G^+}$, one gets:

$$\frac{a_{H^+}}{a_{H_G^+}} = \frac{a_{H^+} + K_e a_{M^+}}{a} \tag{7.70}$$

Replacing $a_{H^+}/a_{H_G^+}$ in the equation for the glass electrode potential by its value from (7.66) gives

$$\varepsilon_G = \varepsilon_G^0 + b^0 \log (a_{H^+} + K_e a_{M^+}) \tag{7.71}$$

where the standard potential of the glass electrode ε_G^0 includes the quantity $RT/F \ln a$, which is constant for a given electrode.

Thus, in a general case the glass electrode potential depends on the activities of the hydrogen ions and alkali metal ions. When

$$a_{H^+} \gg K_e a_{M^+}$$

which is true for acidic solutions and also (owing to the low value of K_e) for neutral and weakly alkaline solutions with a pH value of up to 10-12, Eq. (7.71) simplifies to

$$\varepsilon_G = \varepsilon_G^0 + b^0 \log a_{H^+} = \varepsilon_G^0 - b^0 \text{ pH} \qquad (7.72)$$

In such solutions the glass electrode potential depends only on the hydrogen ion activity; that is why the glass electrode is used as indicator electrode in pH measurements. At

$$a_{H^+} \ll K_e a_{M^+}$$

i.e., in the alkaline region, Eq. (7.67) also simplifies, taking the form

$$\varepsilon_G = \varepsilon_G^{0'} + b^0 \log a_{M^+} \qquad (7.73)$$

where the quantity $\varepsilon_G^{0'}$ includes a term containing the exchange constant

$$2.303 \frac{RT}{F} \log K_e$$

It follows from Eq. (7.73) that for alkaline solutions the glass electrode potential is a function of the alkali cationic activity and it can therefore be employed as indicator electrode for determining the ionic activity of the corresponding alkali metal. When an alkaline solution alone is the source of cations,

$$a_{M^+} = a_{OH^-}$$

and since

$$a_{H^+} a_{OH^-} = K_W$$

then for the alkaline region of solutions, in place of Eq. (7.73), one can write

$$\varepsilon_G = \varepsilon_G^{0''} - 2.303 \frac{RT}{F} \log a_{H^+} = \varepsilon_G^{0''} + b^0 \text{ pH} \qquad (7.74)$$

from which it is seen that for acidic and alkaline solutions the glass electrode potential is a function of hydrogen ion activity. Each region of solutions has its own value of standard potential ε^0 and the slopes of ε^0 vs. pH straight lines in acidic and alkaline regions are equal in magnitude and opposite in sign. The variation of the glass electrode potential with pH is described by a curve with a maximum (Fig. 7.1), the position of which depends on the type of glass used and primarily on its exchange constant. Because of the uncertainty of ε^0 (it depends on the nature of the glass, its treatment, etc.) glass

electrodes should be calibrated against a series of solutions of known pH value.

The procedure for measuring the glass electrode potential is as follows. A glass electrode in the form of a thin membrane, on one side of which is a solution under study and on the other a solution of constant pH[1]), is introduced into the electrochemical system. Then reference electrodes (most often, silver-silver chloride electrodes) are immersed in each of these solutions. The potentials on either side of the membrane are determined by the corresponding exchange reactions; on one side, however, the potential remains constant, while on the other it varies together with the composition of the solution according to the equations derived above. Thus, the glass electrode potential is equal to the potential difference between the two sides of the membrane. If the sides of the membrane were identical, then, with one and the same solution, the glass electrode potential would be zero. But in reality the properties of the glass on both sides of the membrane differ, giving rise to a certain potential difference. This potential difference—the *asymmetry potential* of the glass electrode—is included in the value of its standard potential.

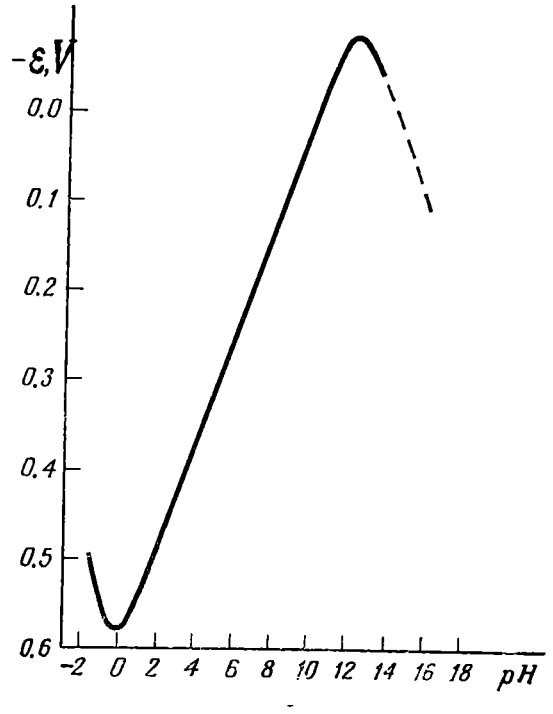


Fig. 7.1. Dependence of the potential of a glass electrode on solution pH

The above consideration of the glass electrode is in accord with the thermodynamic theory of the glass electrode developed by B. Nikolsky (1937) and is based on the concept of the existence of an ion exchange between glass and solution. Similar assumptions were advanced by Dole (1934) in his quantum-mechanical theory of the glass electrode.

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[1]) In some glass electrode designs, instead of a solution of constant pH, use is made of low-melting metals or alloys (e.g., the Wood alloy), a thin layer of which is applied to one side of the membrane. Such glass electrodes are called *metallized.*

7.4. STANDARD ELECTRODE POTENTIALS

7.4.1. THE TABLE OF STANDARD ELECTRODE POTENTIALS

The general equation for the electrode potential (7.14) indicates that at a given temperature the magnitude of the potential of any electrode depends on the composition of the system and its standard potential, which is independent of the activities of the substances taking part in the electrode reaction and is a constant specific to a given electrode. The values of standard potentials for a number of electrodes on the hydrogen scale and the corresponding electrode reactions are presented in Table 7.2.

The standard potentials given in Table 7.2 are referred to $t = 25°C$; their values for other temperatures can be found from the corresponding isothermal temperature coefficients, which are also given in the table. The isothermal coefficients correspond to the reaction

$$Ox^{(z+)} + \left(\frac{z}{2}\right) H_2 = Red + zH^+ \qquad (7.75)$$

occurring in the electrochemical cell

$$M/H_2/Pt/\text{electrolyte (electrode) } M$$

in which both electrodes and the electrolyte are at the same temperature (25°C). Any change of the system emf due to deviations of the temperature from 25°C is primarily determined by the difference in the temperature coefficients of the potentials of the electrode being tested and the standard hydrogen electrode. Since the potential of the standard hydrogen electrode is taken as zero at all temperatures, the emf of the system (7.71) at any specified temperature will be equal to the standard potential of the electrode under study on the hydrogen scale.

From the thermodynamics of electrochemical systems it follows that the first isothermal temperature coefficient reflects the change in the standard entropy during a reaction (7.75) proceeding in a given direction, i.e.,

$$\left(\frac{d\mathcal{E}^0}{dT}\right) = \frac{\Delta S^0}{zF} \qquad (7.76)$$

and the second, the change in the standard molar isobaric heat capacities

$$\left(\frac{d^2\mathcal{E}^0}{dT^2}\right) = \frac{\Delta c_p^0}{zFT} \qquad (7.77)$$

If the isothermal temperature coefficients are known, the standard potential of any electrode at a temperature t different from 25°C can

TABLE 7.2

Standard Electrode Potentials at 25°C and Their Isothermal Temperature Coefficients

Electrode	Electrode reaction	e^0, V	$\left(\frac{de^0}{dT}\right) \times 10^3$, V/deg C
N_3^-/N_2, Pt	$3/2N_2 + e = N_3^-$	−3.2	—
Li^+/Li	$Li^+ + e = Li$	−3.045	−0.534
Rb^+/Rb	$Rb^+ + e = Rb$	−2.925	−1.245
Cs^+/Cs	$Cs^+ + e = Cs$	−2.923	−1.197
K^+/K	$K^+ + e = K$	−2.925	−1.080
Ra^{2+}/Ra	$Ra^{2+} + 2e = Ra$	−2.916	−0.59
Ba^{2+}/Ba	$Ba^{2+} + 2e = Ba$	−2.906	−0.395
Ca^{2+}/Ca	$Ca^{2+} + 2e = Ca$	−2.866	−0.175
Na^+/Na	$Na^+ + e = Na$	−2.714	−0.772
La^{3+}/La	$La^{3+} + 3e = La$	−2.522	+0.085
Mg^{2+}/Mg	$Mg^{2+} + 2e = Mg$	−2.363	+0.103
Be^{2+}/Be	$Be^{2+} + 2e = Be$	−1.847	+0.565
HfO_2, H^+/Hf	$HfO_2 + 4H^+ + 4e = Hf + 2H_2O$	−1.7	—
Al^{3+}/Al	$Al^{3+} + 3e = Al$	−1.662	+0.504
Ti^{2+}/Ti	$Ti^{2+} + 2e = Ti$	−1.628	—
Zr^{4+}/Zr	$Zr^{4+} + 4e = Zr$	−1.529	—
V^{2+}/V	$V^{2+} + 2e = V$	−1.186	—
Mn^{2+}/Mn	$Mn^{2+} + 2e = Mn$	−1.180	−0.08
WO_4^{2-}/W	$WO_4^{2-} + 4H_2O + 6e = W + 8OH^-$	−1.05	—
Se^{2-}/Se	$Se + 2e = Se^{2-}$	−0.77	—
Zn^{2+}/Zn	$Zn^{2+} + 2e = Zn$	−0.7628	+0.091
Cr^{3+}/Cr	$Cr^{3+} + 3e = Cr$	−0.744	+0.468
SbO_2^-/Sb	$SbO_2^- + 2H_2O + 3e = Sb + 4OH^-$	−0.67	—
Ga^{3+}/Ga	$Ga^{3+} + 3e = Ga$	−0.529	+0.67
S^{2-}/S	$S + 2e = S^{2-}$	−0.51	—
Fe^{2+}/Fe	$Fe^{2+} + 2e = Fe$	−0.4402	+0.052
Cr^{3+}, Cr^{2+}/Pt	$Cr^{3+} + e = Cr^{2+}$	−0.408	—
Cd^{2+}/Cd	$Cd^{2+} + 2e = Cd$	−0.4029	−0.093
Ti^{3+}, Ti^{2+}/Pt	$Ti^{3+} + e = Ti^{2+}$	−0.369	—
Tl^+/Tl	$Tl^+ + e = Tl$	−0.3363	−1.327
Co^{2+}/Co	$Co^{2+} + 2e = Co$	−0.277	+0.06
Ni^{2+}/Ni	$Ni^{2+} + 2e = Ni$	−0.250	+0.06
Mo^{3+}/Mo	$Mo^{3+} + 3e = Mo$	−0.20	—
Sn^{2+}/Sn	$Sn^{2+} + 2e = Sn$	−0.136	−0.282
Pb^{2+}/Pb	$Pb^{2+} + 2e = Pb$	−0.126	−0.451
Ti^{4+}, Ti^{3+}/Pt	$Ti^{4+} + e = Ti^{3+}$	−0.04	—
D^+/D_2, Pt	$D^+ + e = {}^1/_2D_2$	−0.0034	—
H^+/H_2, Pt	$H^+ + e = {}^1/_2H_2$	±0.000	±0.000 (+0.871) *
Ge^{2+}/Ge	$Ge^{2+} + 2e = Ge$	+0.01	—
Sn^{4+}, Sn^{2+}/Pt	$Sn^{4+} + 2e = Sn^{2+}$	+0.15	—
Cu^3, Cu^+/Pt	$Cu^{2+} + e = Cu^+$	+0.153	+0.073
Cu^{2+}/Cu	$Cu^{2+} + 2e = Cu$	+0.337	+0.008
$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}/Pt$	$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$	+0.36	—
OH^-/O_2, Pt	$^1/_2O_2 + H_2O + 2e = 2OH^-$	+0.401	−0.44

Table 7.2, continued

Electrode	Electrode reaction	ε^0, V	$\left(\frac{d\varepsilon^0}{dT}\right) \times 10^3$, V/deg C
Cu^+/Cu	$Cu^+ + e = Cu$	+0.521	−0.058
I^-/I_2, Pt	$I_2 + 2e = 2I^-$	+0.5355	−0.148
Te^{4+}/Te	$Te^{4+} + 4e = Te$	+0.56	—
MnO_4^-, MnO_4^{2-}/Pt	$MnO_4^- + e = MnO_4^{2-}$	+0.564	—
Rh^{2+}/Rh	$Rh^{2+} + 2e = Rh$	+0.60	—
Fe^{3+}, Fe^{2+}/Pt	$Fe^{3+} + e = Fe^{2+}$	+0.771	+1.188
Hg_2^{2+}/Hg	$Hg_2^{2+} + 2e = 2Hg$	+0.788	—
Ag^+/Ag	$Ag^+ + e = Ag$	+0.7991	−1.000
Hg^{2+}/Hg	$Hg^{2+} + 2e = Hg$	+0.854	—
Hg^{2+}, Hg^+/Pt	$Hg^{2+} + e = Hg^+$	+0.91	—
Pd^{2+}/Pd	$Pd^{2+} + 2e = Pd$	+0.987	—
Br^-/Br_2, Pt	$Br_2 + 2e = 2Br^-$	+1.0652	−0.629
Pt^{2+}/Pt	$Pt^{2+} + 2e = Pt$	+1.2	—
Mn^{2+}, H^+/MnO_2, Pt	$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	+1.23	−0.661
Tl^{3+}, Tl^+/Pt	$Tl^{3+} + 2e = Tl^+$	+1.25	+0.89
Cr^{3+}, $Cr_2O_7^{2-}$, H^+/Pt	$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	+1.33	−1.263
Cl^-/Cl_2, Pt	$Cl_2 + 2e = 2Cl^-$	+1.3595	−1.260
Pb^{2+}, H^+/PbO_2, Pt	$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	+1.455	−0.238
Au^{3+}/Au	$Au^{3+} + 3e = Au$	+1.498	—
MnO_4^-, H^+/MnO_2, Pt	$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	+1.695	−0.666
Ce^{4+}, Ce^{3+}/Pt	$Ce^{4+} + e = Ce^{3+}$	+1.61	—
SO_4^{2-}, $H^+/PbSO_4$, PbO_2, Pb	$PbO_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_2O$	+1.682	+0.326
Au^+/Au	$Au^+ + e = Au$	+1.691	—
H^-/H_2, Pt	$H_2 + 2e = 2H^-$	+2.2	—
F^-/F_2, Pt	$F_2 + 2e = 2F^-$	+2.87	−1.830

Note. Standard potentials are given here in order of increasing positive value. This table corresponds to the electrochemical series of electrode reactions. It includes the electrochemical series of metals (the so-called Volta series).

* This is the thermal temperature coefficient of the SHE potential.

be calculated from the equation

$$\varepsilon_t^0 = \varepsilon_{25}^0 + \left(\frac{d\varepsilon^0}{dT}\right)(t-25) + \frac{1}{2}\left(\frac{d^2\varepsilon^0}{dT^2}\right)(t-25)^2 \qquad (7.78)$$

Since the second isothermal temperature coefficients are known for a very limited number of electrodes, calculations are made by using an approximate equation, taking into account only the first isothermal coefficient:

$$\varepsilon_t^0 = \varepsilon_{25}^0 + \left(\frac{d\varepsilon^0}{dT}\right)(t-25) \qquad (7.79)$$

For instance, for the Ag^+/Ag electrode at which the following reaction takes place

$$Ag^+ + e = Ag$$

the standard potential at 55°C is equal to

$$\varepsilon^0_{Ag^+/Ag\,(55°C)} = 0.7991 - 1.000 \times 10^{-3}\,(55 - 25) = 0.7691 \text{ V}$$

Knowing the value of the isothermal temperature coefficient of the potential and the thermal temperature coefficient of the standard hydrogen electrode, one can find the thermal temperature coefficient of any electrode:

$$\left(\frac{d\varepsilon^0_{el}}{dT}\right)_T = \left(\frac{d\varepsilon^0_{el}}{dT}\right) + \left(\frac{d\varepsilon^0_H}{dT}\right)_T \qquad (7.80)$$

or, since

$$\left(\frac{d\varepsilon^0_H}{dT}\right)_T = 0.871 \text{ mV/deg C}$$

then

$$\left(\frac{d\varepsilon^0_{el}}{dT}\right)_T = \left(\frac{d\varepsilon^0_{el}}{dT}\right) + 0.871 \text{ mV/deg C}$$

The thermal temperature coefficient corresponds to the change of the emf in a thermogalvanic cell[1], i.e., in an electrochemical system consisting of two identical electrodes immersed in solutions of the same composition but at different temperatures t_1 and t_2. The thermal temperature coefficient is considered positive if the "hot" electrode in a thermogalvanic cell is the positive pole or, in other words, if with rising temperature the electrode potential shifts towards more positive values. For example, for the thermogalvanic system

$$\underset{t_1}{M'/Ag/AgNO_3/Ag/M}\underset{t_2}{}$$

the thermal coefficient will be equal to

$$\left(\frac{d\varepsilon^0_{Ag^+/Ag}}{dT}\right)_T = -1.000 + 0.871 = -0.129 \text{ mV/deg C}$$

that is, in this system the "hot" electrode has a less positive potential.

7.4.2. THE USE OF STANDARD POTENTIALS

Standard potentials are used to resolve many problems associated with chemical equilibrium in solutions. When the electrode potential coincides in magnitude with the standard potential, i.e., when

[1] Here we consider the simplest form of a thermogalvanic cell. In a general case, the electrodes in a thermogalvanic cell may be different in nature and not necessarily reversible. They may be brought into contact with solutions of different composition.

the second term in Eq. (7.14) is equal to zero, any electrode situated lower in the electrochemical series is more oxidized than an electrode situated higher, i.e., closer to the top of the series. When two such electrodes are combined to form an electrochemical system, we will have reduction at the first electrode and oxidation at the second. The process will proceed in the same direction if the active substances of both electrodes are in direct contact and the reaction follows the chemical path. In either case, as a result of the reaction, the composition of the system will change and the electrode potentials will no longer correspond to the standard values. An equilibrium will set in at the moment when the potentials of the two electrodes (or the two electrode reactions) become equal. This state is reached at a definite ratio of the activities of the reacting species, corresponding to the equilibrium constant of the reaction.

Suppose we have redox systems of the type Ce^{3+}, Ce^{4+} and Fe^{2+}, Fe^{3+}. The electrode potential of the first system at 25°C is given by the equation

$$\varepsilon_{Ce^{3+},\,Ce^{4+}} = 1.61 + 0\ 059 \log \frac{a_{Ce^{4+}}}{a_{Ce^{3+}}} \tag{7.81}$$

and that of the second, by

$$\varepsilon_{Fe^{2+},\,Fe^{3+}} = 0.77 + 0\ 059 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \tag{7.82}$$

In a system containing iron and cerium ions an equilibrium will be set up when the two electrode potentials become equal:

$$\varepsilon_{Ce^{3+},\,Ce^{4+}} = \varepsilon_{Fe^{2+},\,Fe^{3+}}$$

Then, on the basis of Eqs. (7.81) and (7.82), one can write

$$1.61 + 0.059 \log \frac{a_{Ce^{4+}}}{a_{Ce^{3+}}} = 0.77 + 0.059 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \tag{7.83}$$

Hence, at equilibrium

$$\frac{a_{Ce^{3+}} a_{Fe^{3+}}}{a_{Ce^{4+}} a_{Fe^{2+}}} = 10^{\frac{1.61-0.77}{0.059}} = 10^{14} \tag{7.84}$$

When a solution containing ceric and cerous ions is added to a solution containing ferric and ferrous ions, the reaction will proceed in the direction of oxidation of the ions of bivalent iron and reduction of those of tetravalent cerium; at equilibrium the iron will be practically completely oxidized to ferric ions, and the cerium reduced to cerous ions. The system Ce^{3+}, Ce^{4+} can be used in chemical volumetric analysis (cerimetry) because of its high oxidation potential.

A similar picture is observed on mixing solutions of Fe^{2+}, Fe^{3+} and Sn^{2+}, Sn^{4+}, where the iron is reduced and the tin is oxidized. At equilibrium, as follows from the magnitudes of standard potentials:

$$\frac{a^2_{Fe^{3+}} a_{Sn^{2+}}}{a^2_{Fe^{2+}} a_{Sn^{4+}}} = 10^{\frac{0.15-0.77}{0.03}} = 10^{-20.7} \qquad (7.85)$$

practically all the dissolved iron will be present as bivalent ions. Solutions of salts of bivalent tin are therefore used for quantitative reduction of ferric to ferrous ions and for other reduction processes.

Analogous phenomena lie at the basis of the process of displacement of metals from solutions of their salts by other metals situated closer to the top of the electrochemical series. This process is called cementation or contact displacement and is widely employed in engineering. In practice, cases of contact displacement of copper from solutions of its simple salts by iron are often encountered. Equating the electrode potentials of partial reactions and substituting the table values of standard potentials, one obtains for the state of equilibrium:

$$\frac{a_{Cu^{2+}}}{a_{Fe^{2+}}} = 10^{-26} \qquad (7.86)$$

Thus, if a copper salt solution is brought into contact with a sufficient amount of metallic iron, the processes of iron dissolution and copper deposition will continue until the ratio of their ionic activities begins to satisfy Eq. (7.86). This equation shows that if the activity of ferrous ions is equal to unity, the activity of copper ions will be as low as 10^{-26}, i.e., the solution will be practically completely free of bivalent copper ions.

If two electrodes are situated close to each other in the electrochemical series, as, for example, Sn^{2+}, Sn^{4+} and Cu^{+}, Cu^{2+}, then the equilibrium constant of a redox reaction will differ little from unity, and when solutions containing such redox couples are mixed, the oxidation-reduction equilibrium is displaced only slightly.

Most electrochemical processes occur in contact with water and air. This is why the position of a given electrode in the electrochemical series relative to the electrodes

$$H^+/H_2,\ Pt$$

and

$$OH^-/O_2,\ Pt$$

(printed in bold type in Table 7.2) is particularly important from the practical and theoretical points of view.

All electrodes with a potential more negative than the hydrogen electrode potential are thermodynamically unstable in aqueous

solutions. Reactions corresponding to such electrodes will proceed spontaneously, resulting in more oxidized substances and simultaneous decomposition of the water with evolution of hydrogen gas. For example, metallic sodium ($\varepsilon^0_{Na^+/Na} = -2.71$ V) should decompose water and pass into the ionic state according to the equation

$$Na + H_2O = Na^+ + \frac{1}{2} H_2 + OH^-$$

or, in acidic media, according to the equation

$$Na + H^+ = Na^+ + \frac{1}{2} H_2$$

The ratio of the activity of sodium ions to that of hydrogen ions at which equilibrium sets in is approximately equal to 10^{93}. Since this ratio is impossible to realize either in acidic solutions, where the activity of hydrogen ions a_{H^+} is close to unity, or in alkaline solutions, in which a_{H^+} is about 10^{-14}, metallic sodium is always unstable when in contact with water.

Similarly, since the standard potential of the redox system Ti^{2+}, Ti^{3+} is considerably more negative than the hydrogen electrode potential ($\varepsilon^0_{Ti^{2+}/Ti^{3+}} = -0.37$ V), in aqueuos solutions of bivalent salts of titanium spontaneous oxidation of Ti^{2+} to Ti^{3+} ions will proceed with simultaneous decomposition of water:

$$Ti^{2+} + H_2O = Ti^{3+} + \frac{1}{2} H_2 + OH^-$$

or, in acidic media,

$$Ti^{2+} + H^+ = Ti^{3+} + \frac{1}{2} H_2$$

All electrodes whose potentials are less positive than the oxygen electrode potential are thermodynamically unstable when in contact with air and water. In such cases spontaneous reaction of oxygen and its conversion into water or hydrogen peroxide is observed with simultaneous oxidation of the corresponding metals or other substances. For example, metallic iron ($\varepsilon^0_{Fe^{2+}/Fe} = -0.44$ V) reacts with the oxygen of the air

$$Fe + \frac{1}{2} O_2 + H_2O = Fe^{2+} + 2OH^-$$

Ions of univalent copper ($\varepsilon^0_{Cu^+/Cu^{2+}} = +0.154$ V) also oxidize spontaneously to bivalent ions

$$2Cu^+ + \frac{1}{2} O_2 + H_2O = 2Cu^{2+} + 2OH^-$$

and metallic copper ($\varepsilon^0_{Cu^{2+}/Cu} = +0.34$ V) goes into solution as bivalent ions, simultaneously reducing oxygen:

$$Cu + \frac{1}{2} O_2 + H_2O = Cu^{2+} + 2OH^-$$

Thus, if an electrode is situated between the hydrogen and oxygen electrodes in the electrochemical series, decomposition of water with evolution of hydrogen is thermodynamically improbable. Since reduction of oxygen is still possible, such an electrode must be thermodynamically unstable in the presence of water and air. But if the aqueous solution is degassed and the air above it is replaced with an inert atmosphere, reduction of oxygen will then be avoided and the electrode will become thermodynamically stable. Under these conditions it is possible to realize a reversible electrode potential and to measure its magnitude against the corresponding reference electrode.

Finally, electrodes with potentials more positive than the potential of the equilibrium oxygen electrode are thermodynamically unstable and will decompose water with evolution of oxygen gas. For example, judging by the value of the standard potential of ceric and cerous ions, which is equal to +1.61 V, the ions of tetravalent cerium must reduce spontaneously with simultaneous decomposition of water and formation of oxygen

$$Ce^{4+} + \frac{1}{2} H_2O = Ce^{3+} + \frac{1}{4} O_2 + H^+$$

To evaluate the thermodynamic stability of electrodes in aqueous solutions, it is convenient to use a diagram of the type shown in Fig. 7.2, which gives the reversible potentials of the oxygen (line *a*) and hydrogen (line *b*) electrodes as a function of hydrogen ion concentration in the range of pH = 0 to 14. The area *1* below the line *b* of equilibrium potentials of the hydrogen electrode corresponds to the region of water decomposition with evolution of hydrogen. The area *3* above the line *a* of equilibrium potentials of the oxygen electrode corresponds to the region of water decomposition with formation of oxygen. Within the area *2* situated between the lines *a* and *b* the water will not decompose; on the contrary, it may be formed from hydrogen and oxygen. In the absence of these gases, electrodes whose potentials are within the area *2* will be thermodynamically stable. Using this diagram, one can easily predict the behaviour of any electrode in aqueous solutions provided that the magnitude of its potential at a given value of pH is known. Figure 7.2 also gives the thermodynamic stability of water at 25°C and atmospheric pressure as a function of the pH of the solution and the value of electrode potential.

In using the data of Table 7.2 it is necessary to keep in mind that the conclusions based on them are the most probable only thermodynamically, indicating only whether a given process is thermodynamically possible. In actual conditions, however, there may be deviations from the conclusions made, and the processes involved may occasionally proceed differently from what would be expected from

general thermodynamic considerations. Such deviations are possible primarily because the thermodynamic equations for electrode potentials lose their meaning when the activities of the reacting species are vanishingly small. If the activity of even one of the reactants is equal to zero, the electrode potentials must become infinitely large in absolute value; this is not observed in actual fact. Each electrode

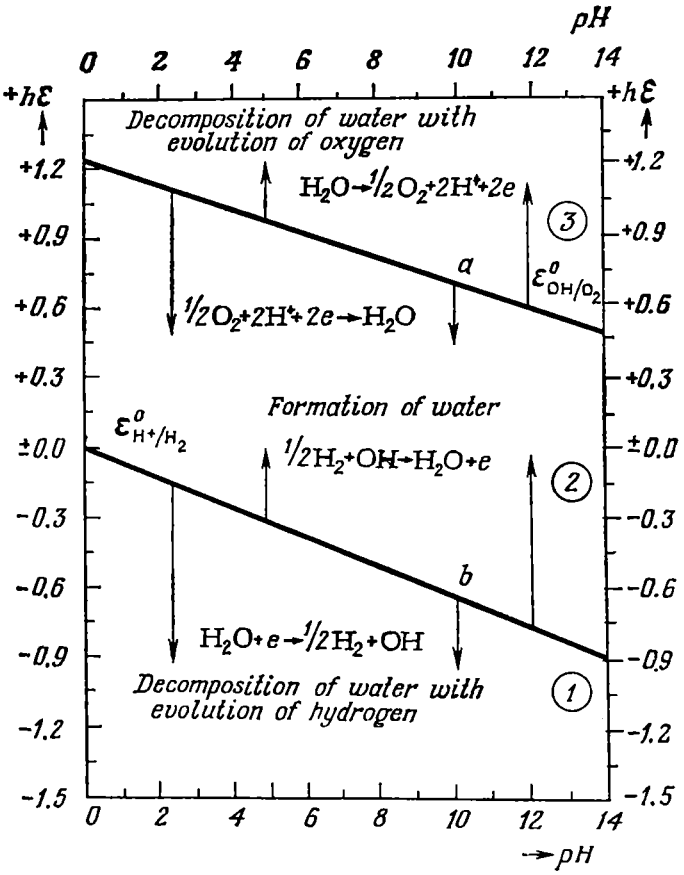


Fig. 7.2. Regions of electrochemical stability of water and electrodes in aqueous solutions

has a limiting value of activity below which the thermodynamic equation of the electrode potential ceases to agree with experiment. But the mechanism of the potential-determining electrode reaction usually changes even before this limiting value is reached; hence, the nature of the electrode itself and the corresponding variation of of the potential with the composition of the system also change. Thus, for most metallic electrodes of the first kind the variation of potential with activity can no longer be described by the corresponding thermodynamic equation if the concentration is below

10^{-6} g-ion/litre. The fact that electrode processes do not always proceed reversibly may also cause deviations in the region where the thermodynamic equation for the equilibrium electrode potential must agree with experiment. As far as irreversible chemical processes proceeding at an appreciable rate are concerned, they are known to defy thermodynamic interpretation. They obey the laws of chemical kinetics. It may turn out that a process, which is thermodynamically probable does not actually take place because of its specific kinetic features. And, finally, departures are also possible associated with phenomena omitted in the general thermodynamic treatment of electrode potentials such as the so-called passivation of electrodes.

CHAPTER 8

Electrochemical Systems (Electrochemical Cells)

8.1. PRINCIPLES OF CLASSIFICATION OF ELECTROCHEMICAL SYSTEMS

Not only can the various electrodes be classified according to the nature of the electrode reaction but also their possible combinations. Three principal types of electrochemical systems, or cells, are distinguished.

Systems of the first type consist of two chemically identical electrodes with one and the same electrode reaction. The emf of such systems would be equal to zero if the physical properties of both electrodes and hence their standard potentials were identical. But if the standard potentials of the electrodes do not coincide owing to the difference in their physical properties, the emf of the system will be different from zero:

$$E = \varepsilon_r^0 - \varepsilon_l^0 = E^0 \tag{8.1}$$

This equation follows from the general thermodynamic equation (7.12). Electrochemical systems, or cells, in which the electrodes differ only in their physical properties and the emf is given by Eq. (8.1) are called *physical cells*. In a physical cell, one electrode, as a rule, is in a more stable and the other in a less stable state under given conditions. The source of electrical energy is the free energy of transition of the electrode from the less to the more stable state.

In systems of the second type there are two electrodes coinciding in their physical properties, qualitative chemical composition and the nature of the electrode reaction, but the activities of one (or several) of the participants in the respective electrode reactions are different. In this case the emf of the system (taking into account the equality of the standard potentials of the electrodes) is given, on the basis of Eq. (7.12), by

$$E = \frac{RT}{zF} \ln \frac{a_{k_2} a_{n_2}}{a_{k_1} a_{n_1}} \tag{8.2}$$

where k and n are the participants in the electrode reactions, with activities different at each of the electrodes. Electrochemical systems in which the electrodes differ only in the activity (concentration) of the participants in the electrode reaction and the emf is determined by Eq. (8.2) are called *concentration cells*. The source of electrical energy in such cells is the energy of transfer of a substance from the greater to the lower activity.

Electrochemical systems of the third type are cells in which the electrodes may differ both in their chemical and physical properties. The emf of a system of this type is expressed by the general equation (7.12). Such electrochemical systems are called *chemical cells.* In these cells, the source of electrical energy is the chemical reactions proceeding in them.

8.2. TYPES OF ELECTROCHEMICAL SYSTEMS

8.2.1. PHYSICAL CELLS

Gravitational Cells. These cells usually consist of two liquid electrodes of different height made of one and the same metal. The electrodes are immersed in a solution of a salt of the given metal. A cell of this type with mercury electrodes of heights h_1 and h_2 ($h_1 > h_2$) dipped into a solution of mercury salt HgA may be represented as

$$\underset{(h_1)}{\mathrm{Hg}}/\mathrm{HgA}/\underset{(h_2)}{\mathrm{Hg}}$$

The electrode of greater height (h_1) has an increased amount of free energy compared with the electrode of smaller height (h_2), and therefore it dissolves to form mercury ions:

$$\underset{(h_1)}{\mathrm{Hg}} \rightarrow \frac{1}{2}\mathrm{Hg}_2^{2+} + e$$

and at the right-hand electrode the mercury ions are discharged and metallic mercury is deposited:

$$\frac{1}{2}\mathrm{H}_2^{2+} + e = \underset{(h_2)}{\mathrm{Hg}}$$

Hence, the overall process in the cell is the transfer of mercury from the higher electrode to the lower one

$$\underset{(h_1)}{\mathrm{Hg}} \rightarrow \underset{(h_2)}{\mathrm{Hg}}$$

This spontaneous process keeps on running until the heights of the two electrodes become equal. Thus, gravitational cells are electrochemical systems in which the mechanical energy due to the difference in the gravity of the electrodes (whence the name of these cells) is transformed into electrical energy as a result of the electrochemical reactions taking place in them. The emf of gravitational cells depends on the height difference and decreases as this difference becomes smaller. The emf of cells of this type is usually very small. For example, for mercury at a height difference of $\Delta h = 100$ cm the emf

is only about 20×10^{-6} V. Some values of the emf for the system

$$\underset{(h_1)}{Hg/Hg_2I_2}, \quad \underset{(h_2)}{KI/Hg}$$

calculated from the height difference Δh, using the relation $E_{cal} = Mg\Delta h/zF$, where M = molecular weight and g = gravity due to acceleration, and measured directly are as follows:

Δh, cm	32	46	113
$E_{cal} \times 10^6$, V	7.2	9.3	22.9
$E_{exp} \times 10^6$, V	7.4	10.5	21.0

The satisfactory agreement between the theoretical and experimental values of emf corroborates the concept of the origin of electrical energy in gravitational cells. The emf of such cells can be raised to several millivolts by creating a larger difference in the gravity of the electrodes, e.g. by centrifuging. In this case the emf will also be very small, only a small fraction of the mechanical energy consumed for the operation of the centrifuge being converted into electrical energy. Although such cells are of no practical importance, they are of interest because the property described points to the possibility of generation of electrical energy in systems with chemically identical electrodes.

Allotropic Cells. The electrode materials in cells of this type are two modifications of the same metal (M_α and M_β) immersed in a solution (or a melt) of its ion-conducting compound. At a given temperature (unless it is the phase transformation temperature at which the two modifications coexist in equilibrium) only one modification of the metal chosen is stable and the other is in a metastable state. An electrode made of a metal in a metastable state (say, M_β) will possess an increased amount of free energy. It plays the role of the negative electrode in the cell and supplies metal ions to the solution:

$$M_\beta = M^{z+} + ze$$

At the electrode prepared from the stable α-modification metal ions are discharged:

$$M^{z+} + ze = M_\alpha$$

Thus, the overall reaction proceeding in the cell

$$M_\beta/MA/M_\alpha$$

consists in the transfer of metal from the metastable modification to the stable one:

$$M_\beta \rightarrow M_\alpha$$

which is an electrochemical transformation of the unstable modification into the stable one. From the free-energy change, which corresponds to an allotropic transformation, one can calculate the emf

of the system or, conversely, the free energy of an allotropic transformation can be determined from the emf, which is relatively easy to measure.

Under certain conditions such cells can be used to determine the temperature of allotropic transformation. If the temperature is raised to a value at which the α-modification is converted to the β-modification, the metal of the two electrodes will be in the same modification, and the emf of the system will be equal (or close) to zero. The emf of the system may be different from zero because the free energy of two electrodes made of a metal of the same modification need not be equal. This is observed, for example, when the electrodes differ in grain size or are subjected to different internal stresses. An electrode made up of smaller crystals or experiencing excessive mechanical stress plays the role of the negative pole of the cell. This electrode dissolves, and the metal is deposited at the other one. Moreover, an emf may appear even when faces of a single crystal of one and the same metal are used as electrodes, because they possess different amounts of free energy. The electrode formed by the face with the greater amount of surface energy will dissolve, and metal ions will be deposited on the crystal face with the smaller amount of surface energy. By measuring the resulting emf one can find the difference in surface energy between faces of a single crystal of the given metal. It should however be stressed that in many cases the potential difference existing between two different samples of one and the same metal should not be identified with the value of the reversible emf.

Electromotive forces arising in the cases considered are usually small; nevertheless, in certain electrochemical reactions, say in corrosion processes, they should be taken into account.

8.2.2. CONCENTRATION CELLS

Concentration Cells of the First Kind. Two types of concentration cells are distinguished: cells of the first and the second kind. Concentration cells of the first kind consist of two electrodes of the same chemical nature but of different activities; both electrodes are immersed in the same solution. A typical example of concentration cells of the first kind is provided by amalgam cells, in which the electrodes differ only in the activity of the metal dissolved in the amalgam:

$$\underset{(a_I)}{M,\ Hg}/MA/\underset{(a_{II})}{M,\ Hg}$$

If $a_I > a_{II}$, the metal dissolves at the left-hand electrode and passes into solution as the corresponding ions:

$$\underset{(a_I)}{MHg} = M^{z+} + ze + Hg$$

The same reaction proceeds at the right-hand electrode but in the opposite direction:

$$M^{z+} + ze + Hg = \underset{(a_{II})}{MHg}$$

The overall cell process consists in transfer of the metal from the concentrated amalgam to the dilute one

$$\underset{(a_I)}{MHg} \rightarrow \underset{(a_{II})}{MHg}$$

and the emf of such a system is given by

$$E = \frac{RT}{zF} \ln \frac{a_I}{a_{II}} \tag{8.3}$$

In amalgam cells, this process goes on while there is a difference in the concentrations (activities) of the amalgams used as electrodes.

An example of an amalgam cell is provided by a cell consisting of potassium amalgams of different activities and a solution of potassium chloride

$$\underset{(a_I)}{K,\ Hg}/KCl/\underset{(a_{II})}{K,\ Hg}$$

The emf of this system is determined by the formula

$$E = b^0 \log \frac{a_I}{a_{II}}$$

Since metal ions are always positively charged, the emf of the amalgam cell as written will be greater than zero. The fundamentals of the theory of amalgam cells were worked out by V. Tyurin (1890).

Concentration cells of the first kind may also be exemplified by simple gas systems consisting of two identical gas electrodes at different pressures. The emf's of such systems can be found from the mechanical work done in transferring one mole of gas from the high pressure P' to the low pressure P'':

$$E = \frac{RT}{zF} \ln \frac{P'}{P''} \tag{8.4}$$

For example, the emf of the gaseous hydrogen cell

$$\underset{(P'_{H_2})}{H_2,\ Pt}/HCl/\underset{(P''_{H_2})}{H_2,\ Pt}$$

is given by the equation

$$E = \frac{RT}{2F} \ln \frac{P'_{H_2}}{P''_{H_2}} \tag{8.5}$$

In the cell as written, the hydrogen gas is ionized at the left-hand electrode, while at the right-hand electrode the hydrogen ions are

discharged and the hydrogen formed is transferred to the gas phase. The positive electric current flows within the cell from left to right and, according to the International convention, the cell emf will be positive.

The emf of a chlorine gas cell of the type

$$\underset{(P'_{Cl_2})}{Cl_2,\ Pt}/HCl/\underset{(P''_{Cl_2})}{Cl_2,Pt}$$

is given by the equation

$$E = -\frac{RT}{2F}\ln\frac{P'_{Cl_2}}{P''_{Cl_2}} \tag{8.6}$$

If $P' > P''$, then the reaction at the left-hand electrode is the ionization of chlorine resulting in negatively charged chloride ions. At the right-hand electrode, the chloride ions are discharged and the chlorine molecules formed are transferred to the gas phase. The positive current flows from right to left and, according to the International convention, the emf of this cell is negative[1]. Equation (8.4) indicates that for gases such as hydrogen and chlorine with $z = \pm 2$ the emf of a gas cell at a pressure ratio of $P'/P'' = 10$ and at 25°C is about 0.03 V. For an oxygen gas cell ($z = -4$) under the same conditions the emf is equal to 0.015 V.

Concentration Cells of the Second Kind. Cells of this type consist of two identical electrodes immersed in solutions of the same electrolyte of different activities. Depending on the ions with respect to which the electrodes are reversible, concentration cells of the second kind are classified as *cationic*, e.g.

$$\overset{\text{I}}{K,\ Hg}/KCl/\underset{(a_I)\ (a_{II})}{\overset{\text{II}}{KCl/K,\ Hg}}$$

and *anionic*, e.g.

$$\underset{(a_I)\ (a_{II})}{Ag,\ AgCl/HCl\ \ HCl/AgCl,\ Ag}$$

The process giving rise to an emf in cells of this type is the transfer of the electrolyte from the concentrated to the dilute solution; such cells are therefore also known as *concentration cells with transference* (or *transport*). They may also be called *concentration cells with a liquid junction* as there is a boundary between the two solutions, across which ions are transported and a diffusion potential develops.

Consider, as an example, the generation of an emf in anionic cells. If $a_I > a_{II}$, the reaction at the left-hand electrode is

$$Ag + Cl^-_I = AgCl + e$$

[1] The negative value of emf follows from the fact that here $z = -2$.

and ions are transferred according to their transport numbers ($t_+H_I^+ + t_-Cl_I^-$). As a result of the electrode reaction, a molecule of silver chloride is formed, for which one g-ion of chloride ions is used. At the same time, t_- g-ions of chloride ions migrate to the electrode on the left, thus partially compensating the loss of chloride ions. The net loss of chloride ions when one faraday of electricity is passed through the cell is

$$-(1 - t_-)\,Cl_I^- = -t_+Cl_I^-$$

The region around the electrode will lose t_+ g-ions of hydrogen, and so the amount of hydrogen chloride will be reduced by t_+ gram-equivalents.

The same processes will take place at the right-hand electrode but in the opposite direction: first, the conversion of silver chloride into metallic silver and chloride ions:

$$AgCl + e = Ag + Cl_{II}^-$$

and, second, the transport of ions:

$$t_+H_{II}^+ - t_-Cl_{II}^-$$

As a result, the amount of hydrogen chloride at the right-hand electrode will increase by t_+ gram-equivalents.

The sum of all the electrode processes gives the general equation for the electrochemical reaction in the anionic cell:

$$t_+H_I^+ + t_+Cl_{II}^- \rightarrow t_+H_{II}^+ + t_+Cl_{II}^- \qquad (8.7)$$

Thus, the source of electrical energy in the concentration cell under consideration is the transfer of t_+ gram-equivalents of hydrogen chloride from the more concentrated to the more dilute solution. Using Eq. (7.7) in combination with Eq. (8.7), we obtain the expression for the emf of an anionic concentration cell of the second kind:

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H^+_{(I)}}^{t_+} a_{Cl^-_{(I)}}^{t_+}}{a_{H^+_{(II)}}^{t_+} a_{Cl^-_{(II)}}^{t_+}} \qquad (8.8)$$

or

$$E = t_+ \frac{RT}{F} \ln \frac{a_{H^+_{(I)}} a_{Cl^-_{(I)}}}{a_{H^+_{(II)}} a_{Cl^-_{(II)}}} \qquad (8.9)$$

since $E^0 = \varepsilon_1^0 + \varepsilon_2^0$ must be equal to zero for a system with two identical electrodes connected in opposition ($\varepsilon_1^0 = -\varepsilon_2^0$).

Using Eq. (2.4) relating the mean ionic activity of an electrolyte to the activities of its individual ions, one can write

$$a_+a_- = a_\pm^2$$

and obtain, in place of (8.9),

$$E = 2t_+ 2.303 \frac{RT}{F} \log \frac{a_{\pm HCl_{(I)}}}{a_{\pm HCl_{(II)}}} \qquad (8.10)$$

Analogously, one can deduce the equation for the emf of a cationic concentration cell with transport. For example, for an amalgam cell of the type

$$\underset{(a_I)}{\overset{I}{K,\ Hg/KCl}} \ \vdots \ \underset{(a_{II})}{\overset{II}{KCl/K,\ Hg}}$$

the following equation is valid:

$$E = -2t_- 2.303 \frac{RT}{F} \log \frac{a_{\pm KCl_{(I)}}}{a_{\pm KCl_{(II)}}} \qquad (8.11)$$

From Eqs. (8.10) and (8.11) it follows that by measuring the emf of a concentration cell with a liquid junction at different concentrations one can find the transport numbers of the ions.

When the general thermodynamic equation for the emf of reversible electrochemical systems is used to define the emf of concentration cells with transport, the equation is simplified. The value of the standard emf E^0 is omitted and only the term characterizing the effect of the concentration of the reactants on the emf is retained.

8.2.3. CHEMICAL CELLS

Chemical cells are usually subdivided into simple and complex cells. In simple chemical cells one electrode is reversible with respect to the cations of the electrolyte and the other to the anions. In complex cells this condition is not observed.

Simple Chemical Cells. In a hydrogen-oxygen cell of the type

$$H_2,\ M/H_2O/O_2,\ M$$

the source of electrical energy is the chemical energy of the reaction between hydrogen and oxygen which results in the formation of water:

$$H_2 + \frac{1}{2} O_2 = H_2O$$

Combining this reaction with Eq. (7.7), we obtain the following expression for the emf of the hydrogen-oxygen cell

$$E = E^0 + \frac{RT}{2F} \ln P_{H_2} P_{O_2}^{1/2} \qquad (8.12)$$

The same equation can be obtained by considering the partial electrode reactions. The reaction occurring at the hydrogen electrode is the ionization of hydrogen

$$H_2 = 2H^+ + 2e$$

and the reaction at the oxygen electrode is the ionization of oxygen with the formation of hydroxyl ions:

$$\frac{1}{2}O_2 + H_2O + 2e = 2OH^-$$

The overall cell reaction is

$$H_2 + \frac{1}{2}O_2 + H_2O = 2H^+ + 2OH^-$$

from which, taking into account Eq. (7.7), we have

$$E = E^{0'} + \frac{RT}{2F}\ln\frac{P_{H_2}P_{O_2}^{1/2}a_{H_2O}}{a_{H^+}^2 a_{OH^-}^2}$$

This equation can be transformed by putting $a_{H_2O} = 1$ and taking into account that

$$a_{H^+}\, a_{OH^-} = K_W$$

The result of this transformation is

$$E = E^{0'} - \frac{RT}{F}\ln K_W + \frac{RT}{2F}\ln P_{H_2}P_{O_2}^{1/2} \qquad (8.13)$$

Equation (8.13) coincides with Eq. (8.12) at $E^0 = E^{0'} - RT/F \ln K_W$. At 25°C

$$E^0 = \varepsilon^0_{H^+/H_2} + \varepsilon^0_{OH^-/O_2} - \frac{RT}{F}\ln K_W = 0.00 + 0.41 - 0.0592 \log 10^{-14}$$

whence

$$E^0 = 0.00 + 0.41 + 0.83 = 1.24 \text{ V}$$

and

$$E = 1.24 + 0.03 \log P_{H_2}P_{O_2}^{1/2} \qquad (8.14)$$

Equation (8.14) shows that the emf of the hydrogen-oxygen cell depends on the partial pressures of hydrogen and oxygen, increasing with pressure by the logarithmic law. At the same time the emf is independent of the pH of the solution and must be the same in pure water and in alkaline or acidic solutions. As the electrical conductance of pure water is very low, alkaline solutions, predominantly those of KOH, are used in real cells. It would therefore be more correct to write the hydrogen-oxygen cell as

$$M_1,\ H_2/KOH/O_2,\ M_2$$

Today, in connection with the problem of direct conversion of the chemical energy of fuels into electrical energy, cells of this type are of great interest to researchers.

Another example of a simple chemical cell is the standard Weston cell:

$$Cd,\ Hg/CdSO_4/Hg_2SO_4,\ Hg$$

the emf of which is extremely stable and has a small temperature coefficient. In the Weston cell, the left-hand electrode is reversible with respect to cadmium ions

$$Cd = Cd^{2+} + 2e$$

and the right-hand one to sulphate ions

$$Hg_2SO_4 + 2e = 2Hg + SO_4^{2-}$$

The overall reaction in the cell may be written as

$$Cd + Hg_2SO_4 = Cd^{2+} + SO_4^{2-} + 2Hg$$

From this it follows (taking into account that the activities of the solid substances involved are constant) that the emf of the standard Weston cell can be described by the equation

$$E = E^0 - \frac{RT}{2F} \ln a_{Cd^{2+}} a_{SO_4^{2-}} = E^0 - \frac{RT}{E} \ln a_{\pm CdSO_4} \qquad (8.15)$$

Consequently, the emf of this cell is governed by the activity of the cadmium sulphate solution. In practical measurements of the emf of systems under study by the Poggendorff compensation method use is most commonly made of the Weston cell in which the electrolyte is a saturated solution of cadmium sulphate. The amalgam electrode in this cell contains 12.5 per cent of cadmium. The emf of the saturated Weston cell at near-room temperature can be determined from the equation

$$E_t = 1.0183 - 4.0 \times 10^{-5} (t - 20) \qquad (8.16)$$

A further example of a simple chemical cell is the lead, or acid, accumulator

$$Pb,\ PbSO_4/H_2SO_4/PbO_2,\ Pb$$

The cell consists of two electrodes of the second kind: a lead-sulphate electrode, which is reversible with respect to sulphate ions, and a lead-dioxide electrode reversible with respect to hydroxyl ions and hence (like any metal-metal oxide electrode) to hydrogen ions. The current-producing reactions taking place in the cell may be represented as follows:

(a) at the lead-sulphate electrode

$$Pb + SO_4^{2-} = PbSO_4 + 2e$$

(b) at the lead-dioxide electrode

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e = PbSO_4 + 2H_2O$$

(c) the overall cell reaction

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} = 2PbSO_4 + 2H_2O$$

The emf of the cell is thus given by

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{H^+}^4 a_{SO_4^{2-}}^2}{a_{H_2O}^2} = E^0 + \frac{RT}{F} \ln \frac{a_{H^+}^2 a_{SO_4^{2-}}}{a_{H_2O}} \qquad (8.17)$$

Since

$$a_{H^+}^2 a_{SO_4^{2-}} = a_{H_2SO_4}$$

where $a_{H_2SO_4}$ is the total activity of H_2SO_4 we can write for the emf of the lead accumulator, in place of Eq. (8.17),

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H_2SO_4}}{a_{H_2O}} \qquad (8.18)$$

or, at 25°C,

$$E = 2.04 + 0.059 \log \frac{a_{H_2SO_4}}{a_{H_2O}} \qquad (8.19)$$

In lead accumulators use is made of concentrated solutions of sulphuric acid, and therefore the activity of water a_{H_2O} is not constant here and cannot be included in the measured emf.

The current-producing processes lying at the basis of Eq. (8.18) are in accord with the so-called theory of double sulphation developed by Gladstone and Tribe. According to this theory both electrodes are converted into lead sulphate on discharge. When they become identical in chemical composition, i.e., when they are both transformed to electrodes of the second kind, $SO_4^{2-}/PbSO_4$, Pb, the cell emf practically falls down to zero. The product of the electrode reactions—solid lead sulphate—is capable of adhering to the electrode surface. Therefore, when a current flows in the opposite direction (if an external source of direct current is connected to the cell), the reactions proceed from right to left, recovering the initial current-producing substances (metallic lead and lead dioxide). After this process is complete, the electrochemical cell can again operate as a source of electrical energy, i.e., it is capable of functioning as an electrochemical accumulator of electrical energy. These discharging and charging cycles may repeat many times, the original state of the system being recovered after each new charging. Such accumulators are therefore sometimes called *secondary cells*, in contrast to primary cells (e.g. the Weston cell) in which the energy of chemical reactions can be used but once.

The cell discussed above was the first lead accumulator. It was designed by Planté in 1859 on the basis of the idea suggested by Jakobi. Later, in the 20th century, alkaline accumulators were devised, viz. nickel-iron (Edison), nickel-cadmium (Jungner) and silver-zinc cells (André).

Complex Chemical Cells. Examples of this type of cells are the primary Daniell-Jakobi and Leclanché cells.

The Daniell-Jakobi cell may be schematically represented as

$$Zn/ZnSO_4 | CuSO_4/Cu$$

The reaction taking place in the cell is

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$

The left-hand electrode, the negative pole of the cell, is reversible with respect to zinc ions, and the electrode on the right, the positive pole, with respect to copper ions. The emf of the cell is therefore determined by the ratio of the activities of copper and zinc ions:

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{Cu^{2+}}}{a_{Zn^{2+}}} \tag{8.20}$$

In this cell there is a boundary between the two solutions, across which a diffusion potential is developed. The equations for the chemical reaction and the emf of the Daniell-Jakobi cell are in fact more complicated than those given above. But since the mobilities of copper and zinc ions do not differ considerably and the concentrations of copper and zinc sulphates are nearly equal, the diffusion potential plays no significant part in the generation of an emf in this cell.

For the Leclanché cell

$$Zn/NH_4Cl,\ ZnCl_2/MnO_2,\ C$$

the probable current-producing reaction may be written as

$$Zn + 2NH_4Cl + 2MnO_2 = Zn(NH_3)_2Cl_2 + Mn_2O_3 + H_2O$$

The theory of the operation of the Leclanché cell has been insufficiently worked out so far.

Double Chemical Cells. In double chemical cells two identical simple cells of different electrolyte activities have a common electrode and are thus electrically combined into a single cell via an electronic conductor. For example, two simple cells consisting of a silver-silver chloride and a hydrogen electrode each can be joined to form a double cell with a common hydrogen electrode:

$$\underset{(a_I)}{\overset{I}{Ag,\ AgCl/HCl/H_2}},\ Pt,\ \underset{(a_{II})}{\overset{II}{H_2/HCl/AgCl,\ Ag}}$$

The same reaction takes place in each single cell:

$$Ag + H^+ + Cl^- = AgCl + \frac{1}{2} H_2$$

but in opposite directions. If $a_I > a_{II}$, then in the first cell the reaction proceeds from left to right, and in the second, from right to left:

$$Ag + H_I^+ + Cl_I^- = AgCl + \frac{1}{2} H_2$$

and

$$AgCl + \frac{1}{2} H_2 = Ag + H_{II}^+ + Cl_{II}^-$$

The overall process is equivalent to the transfer of 1 g-ion of hydrogen and 1 g-ion of chloride ions from the first cell to the second:

$$H_I^+ + Cl_I^- \rightarrow H_{II}^+ + Cl_{II}^-$$

though actually there is no transport in this system because of the absence of a boundary between the solutions, and the change in the amount of hydrochloric acid is caused not by ion transport but by the chemical reactions taking place in the cell. According to the equation for the reaction involved, the emf of the cell is given by

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H_{(I)}^+} a_{Cl_{(I)}^-}}{a_{H_{(II)}^+} a_{Cl_{(II)}^-}} \tag{8.21}$$

Here E^0 is the standard emf and is equal to zero since the same reaction occurs in the two single cells but in opposite directions. On one side of the hydrogen electrode (which is common for both cells) the cathodic process $H^+ + e = {}^1/_2 H_2$ takes place, and on the other, the anodic process ${}^1/_2 H_2 = H^+ + e$. Such electrodes are called *bipolar electrodes*; they find wide use in the electrochemical industry. Taking into account that $E = E_I - E_{II}$ and substituting the mean ionic activity of the acid for individual ionic activities, we can write, in place of (8.21),

$$E = E_I - E_{II} - 2 \frac{RT}{F} \ln \frac{a_{\pm HCl_{(I)}}}{a_{\pm HCl_{(II)}}} \tag{8.22}$$

A double chemical cell resembles a concentration cell of the second kind in the nature of the process involved and in the form of the equation for the emf. In double chemical cells, however, there is no liquid junction between the solutions and so the nuisance of diffusion potentials is avoided. A comparison of the emf of a double chemical cell with that of a concentration cell of the second kind with the same electrolyte enables determination of its transport numbers because in Eq. (8.10), as distinct from Eq. (8.22), the prelogarithmic factor includes the transport number of the cation. By comparing the emf of a double chemical cell with that of the corresponding simple cell, one can find, with great accuracy, the standard potentials of its electrodes as well as the activity coefficients of the electrolytes.

Consider, as an example, the use of double cells for determining the standard potential of a silver-silver chloride electrode and the mean activity coefficient for hydrochloric acid. Suppose that the activities of the hydrogen and chloride ions in cell I and hence the mean activity of the hydrochloric acid are equal to unity, and the hydrogen gas pressure is one atmosphere. The emf of this cell will correspond to its standard emf, which is equal to the difference between the standard potentials of the hydrogen and silver-silver chloride electrodes[1]:

$$E_{\text{I}} = E_{\text{I}}^0 = \varepsilon^0_{\text{H}^+/\text{H}_2} - \varepsilon^0_{\text{Cl}^-/\text{AgCl, Ag}} \tag{8.23}$$

but $\varepsilon^0_{\text{H}^+/\text{H}_2} = 0$ and therefore

$$E_{\text{I}} = -\varepsilon^0_{\text{Cl}^-/\text{AgCl, Ag}}$$

The total emf of a double cell is determined in this case by the equation

$$E = -\varepsilon^0_{\text{Cl}^-/\text{AgCl, Ag}} - E_{\text{II}} = -\frac{2RT}{F} \ln a_{\pm\text{HCl}_{(\text{II})}} \tag{8.24}$$

Taking into account that

$$a_\pm = m_\pm f_\pm$$

one can write, in place of Eq. (8.24),

$$-\varepsilon^0_{\text{Cl}^-/\text{AgCl, Ag}} - E_{\text{II}} = -2\frac{RT}{F} \ln m_{\pm\text{HCl}_{(\text{II})}} - 2\frac{RT}{F} \ln f_{\pm\text{HCl}_{(\text{II})}} \tag{8.25}$$

or, rearranging,

$$\varepsilon^0_{\text{Cl}^-/\text{AgCl, Ag}} - 2\frac{RT}{F} \ln f_{\pm\text{HCl}_{(\text{II})}} = -E_{\text{II}} + 2\frac{RT}{F} \ln m_{\pm\text{HCl}_{(\text{II})}} \tag{8.26}$$

The value of E_{II} at different molalities of the solution, $m_{\pm\text{HCl}_{(\text{II})}}$, is obtained by direct measurement of the emf of a simple chemical cell[2]

$$\underset{(m_\pm)}{\text{Pt, H}_2/\text{HCl/AgCl, Ag}}$$

The value of the right-hand side of Eq. (8.26) may therefore be regarded as known for any molality $m_{\pm\text{HCl}_{(\text{II})}}$; at any value of $m_\pm$, the

---

[1] The equilibrium potential of the silver-silver chloride electrode on the hydrogen scale is defined as the emf of the cell Pt, H_2/HCl/AgCl, Ag. This notation is reversed for cell I, i.e., the hydrogen electrode potential is expressed with respect to the silver-silver chloride electrode, this leading to Eq. (8.23).

[2] The emf of electrochemical cells is usually measured by the Poggendorff compensation method. The principle of this method is explained in textbooks on physical chemistry. A detailed description can be found in manuals on physical chemistry and electrochemistry.

two sides of Eq. (8.26) are equal. If the quantity $(-E_{II} + 2RT/F \ln m_{\pm HCl(II)}) = E'_{II}$ is plotted against $m^{1/2}_{\pm HCl(II)}$, a curve will result similar to the one given in Fig. 8.1. Extrapolation of this curve up to its intersection with the ordinate yields the value of $\varepsilon^0_{Cl^-/AgCl, Ag}$ since as $m_\pm \to 0$ the quantity $f_\pm$ tends to unity and $\log f_\pm \to 0$ and, hence, the left-hand side of Eq. (8.26) will be equal

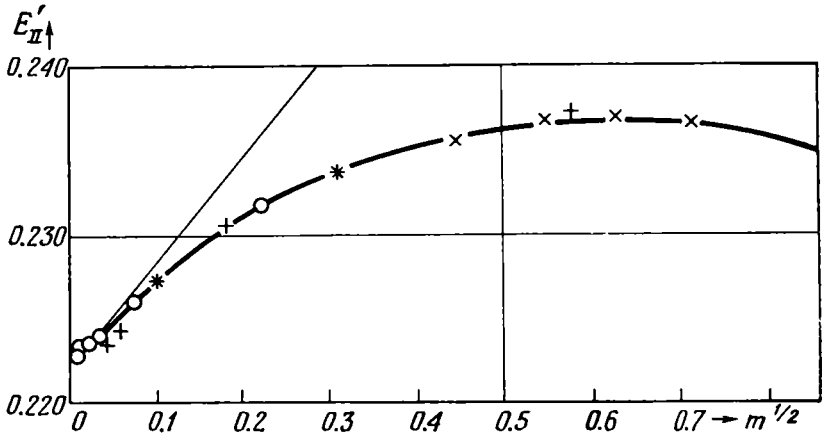


Fig. 8.1. The graphical determination of the standard potential of a silver-silver chloride electrode from changes in the emf's of chemical cells

to the standard potential of the silver-silver chloride electrode on the hydrogen scale. At 25°C the value of the standard potential of the silver-silver chloride electrode obtained in this way is

$$\varepsilon^0_{Cl^-/AgCl, Ag} = 0.2224 \pm 0.00016 \text{ V}$$

Now that the value of the standard potential of the silver-silver chloride electrode is known, one can find the ionic activity for hydrochloric acid by using the equations for the emf of a simple chemical cell and the potential of the silver-silver chloride electrode. Since the relation between the cell emf and the molality of the electrolyte is not linear, for exact extrapolation one has to measure the value of emf in very dilute solutions. The solutions used shall be pure and the experiment must be carried out very carefully. Other methods of extrapolation have been proposed which make use of the theoretical or empirical equations for the activity coefficient. This enables one to avoid the difficulties indicated and to restrict himself to measurements of the emf in not very dilute solutions.

Many of the standard potentials listed in Table 7.2 have been determined by this method. In those cases when direct measurement was impossible, the values were found from thermochemical data.

8.3. POTENTIOMETRY

Potentiometry, like conductometry, is an electrochemical method of analysis widely used in scientific research and in control of various technological processes. It is based on the dependence of electrode potentials on the composition of the solution. As distinct from the conductometric method, the potentiometric technique is used to measure a specific property of solutions—the activity of a given ionic species. It should be kept in mind however that the activity of ions of a given type depends not only on their concentration but also on the ionic strength of the solution, i.e., on its general composition. In this sense, activity, like electrical conductance, is an integral property of the solution.

The potentiometric method can be used to determine not only the activity of the ions present in a given solution under given conditions, but also the total concentration of these species, no matter whether they are present as free ions or make part of the corresponding compounds. In the first case one speaks of direct potentiometry (ionometry), and in the second, of potentiometric titrations. Combining the results obtained by the two methods, one can determine the dissociation constant of a given electrolyte. For example, in an aqueous solution of acetic acid, as a result of incomplete electrolytic dissociation

$$CH_3COOH = CH_3COO^- + H^+$$

part of the acid is present in the ionized state and the other part in the form of undissociated molecules. Direct potentiometry, or ionometry, yields data on the content of free hydrogen ions and hence the concentration of dissociated molecules of acetic acid. In potentiometric titration, which is conducted in much the same way as ordinary volumetric titration except that the electrode potential is used as indicator, the hydrogen ions are made to combine into water by adding hydroxyl ions, and the equilibrium of the dissociation reaction is shifted to the right until all the acid is titrated.

In direct potentiometry, use is made of electrodes of accurately known standard potential which are strictly reversible with respect to the ionic species to be determined. For example, to measure the hydrogen ion concentration (pH value) one should make use of such indicator electrodes as the hydrogen, quinhydrone or glass electrode; with certain conditions observed and in a definite range of pH each of these electrodes strictly obeys the equation

$$\varepsilon = \varepsilon^0 - b^0 \mathrm{pH}$$

Metal-metal oxide electrodes (e.g. the antimony electrode) can also be used for pH measurements provided they have been calibrated against buffer solutions of known pH[1]. The second electrode (the

[1] A glass electrode must also be calibrated.

reference or comparison) is usually a half-cell of known potential, say, the hydrogen or calomel electrode. Measures must be taken to eliminate possible diffusion potentials so that the measured emf corresponds only to the potential difference between the indicator electrode and the reference electrode.

In potentiometric titrations, indicator electrodes need not meet the above requirements. In this case electrodes must only provide a regular change of the potential with concentration of the ions introduced or to be determined. The reference electrode may be either the internal or the external electrode immersed, together with the indicator electrode, in the test solution. It is necessary that the potential of the reference electrode either remain constant during titration or change differently from that of the indicator electrode. Since in potentiometric titrations the potential of the indicator electrode need not be determined, no measures are taken to eliminate diffusion potentials.

The principle of potentiometric titrations may be illustrated by the following example. Suppose a solution of hydrochloric acid is to be titrated with a solution of sodium hydroxide. By measuring the potential of the indicator electrode one can (assuming that the concentrations are equal to the activities and neglecting the effect of electrostriction) trace the variation of the hydrogen ion concentration during the titration. It can be seen from Fig. 8.2 that the greatest change of the indicator electrode potential is observed near the equivalence point. The point of inflection on the potentiometric titration curve corresponds to the volume of alkaline solution required for the acid to be completely neutralized. If potentiometric titration is carried out with an external reference electrode (or with a reference electrode dipped into the titrate, provided that its potential undergoes no change during the titration), curve *1* in Fig. 8.2 will correspond to the change of the emf of the electrode pair (the indicator and the reference electrode). But if the potential of the internal reference electrode does not remain constant in the course of titration and changes, for example, in accord with curve *2*, then the emf of such a pair of electrodes will vary according to curve *3*. The highest value of emf is observed near the equivalence point and a maximum indicating the end point of titration will appear on curve *3*. With such systems one can, instead of using a potentiometer to record the emf, directly measure the current intensity (noncompensation potentiometric titration). The greatest deflection of the pointer of the measuring instrument (e.g. a high-ohmic galvanometer) coincides with the maximum value of emf and hence with the equivalence point. The potential jump near the equivalence point in acidimetric titrations is the more pronounced, the higher the strengths of the acid and base taking part in the neutralization reaction and the higher their concentrations.

In a similar way, one can carry out titrations based on precipitation, complex-formation and redox reactions. In the case of precipitation and complex-forming reactions the indicator electrode must be reversible with respect to one of the ionic species present in the precipitate or complex ion formed. For example, in the titration of a solution of silver nitrate with sodium chloride resulting in the formation of a silver chloride precipitate, the following electrodes may be used as an indicator electrode: metallic silver (an electrode of the

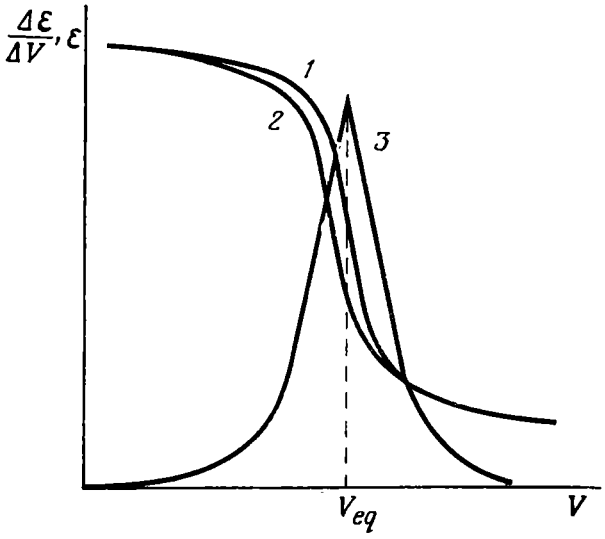


Fig. 8.2. Typical curves of potentiometric titration

first kind reversible with respect to Ag^+ ions); the silver-silver chloride electrode (an electrode of the second kind reversible with respect to Cl^- ions); or the chlorine electrode (a gas electrode reversible with respect to Cl^- ions), which is less convenient to use. The potential change near the equivalence point, i.e., the accuracy, or sensitivity, of the titration will in this case increase with decreasing solubility of the precipitate formed. For instance, when silver ions are titrated with iodide ions, the sensitivity of the method will increase in comparison with the reaction just considered because the solubility of silver iodide ($K_{AgI} = 10^{-16}$) is lower than that of silver chloride ($K_{AgCl} = 10^{-10}$).

In potentiometric titrations based on complex formation the accuracy of the method increases with decreasing dissociation constant (instability constant) of the complex ion formed. In oxidimetric titrations a smooth platinum plate is used as indicator electrode. The potential change near the equivalence point and hence the sensitivity of the titration increases with increasing difference in the standard potentials of the redox systems in the test solution (titrate) and in the standard solution (titrant).

An advantage of potentiometric titrations over the conventional volumetric titration is its objectivity and applicability in the analysis of coloured solutions. Moreover, one can follow the course of the titration and all possible transformations by measuring changes of electrode potential. And, finally, one can determine potentiometrically two (in some cases even three) species of particles—molecules or ions—simultaneously present in the solution. When employed for production control and automatic control of technological processes, potentiometry again has a number of additional advantages over other techniques. It provides uninterrupted control since the indicator electrode can be placed directly into the reaction space. Besides, the potential difference (or the current intensity determined by it) serves as a signal indicating a change in the state of the system being controlled, which is convenient for transmitting the signal to controllers and actuating mechanisms.

CHAPTER 9

The Mechanism of Buildup of Electromotive Force and the Nature of Electrode Potentials

The application of the laws of thermodynamics to electrochemical systems enables one to establish a quantitative relationship between the electrical energy of electrochemical systems and the change of the chemical energy of the current-producing chemical reactions taking place in these systems. The chemical energy of current-producing reactions as a source of electrical energy in electrochemical systems is correctly defined by thermodynamics. But, being a science dealing with general laws, thermodynamics is incapable of indicating the paths and mechanism of conversion of chemical energy into electrical, the parts of which the value of emf is composed, and the nature of the electrode potential.

A more complete picture of electrode equilibrium can be obtained by applying, along with thermodynamics, the molecular-kinetic theory to electrochemical systems.

9.1. ELECTROMOTIVE FORCE [AND ELECTRODE POTENTIAL AS THE SUMS OF INDIVIDUAL POTENTIAL DIFFERENCES]

9.1.1. POTENTIAL DIFFERENCES IN ELECTROCHEMICAL SYSTEMS

Potential differences may arise across the boundary between any two phases, though the mechanism of their formation is not necessarily the same in each particular case and is dependent on the nature of contiguous phases. An electrochemical system (Fig. 9.1) may contain the following phases:

(a) solid metallic phases—two electrodes and the external circuit;

(b) liquid phases—solutions in contact with the electrodes; there may be either two phases when the electrolyte is dissolved in two immiscible solvents, or a single phase when one solvent (e.g. water) is used;

(c) a gas phase in contact with the solutions and electrodes (a phase resembling vacuum in properties).

As is known, the potential difference between two points is defined by the electrical work required to transport a unit charge from one point to the other. If both points are in the same phase, the work

of charge transfer will be only electrical and the potential between the two points selected can be determined. But if the points are in two different phases, the transfer of a unit charge from one point to the other will involve not only electrical but also chemical work since the chemical potentials of this charged species are not equal in

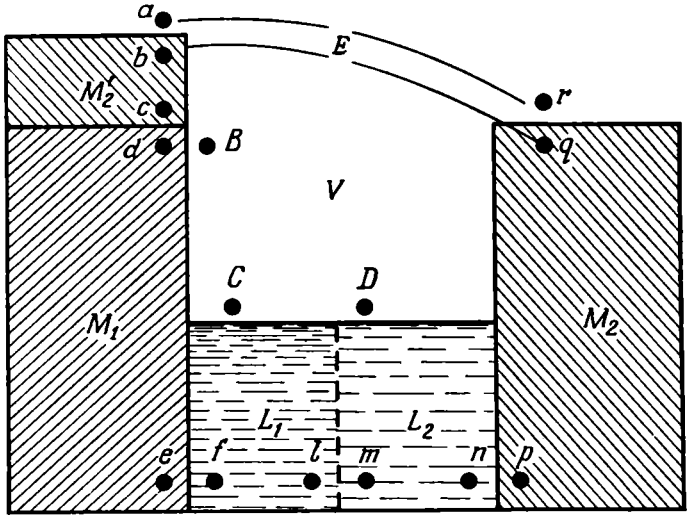


Fig. 9.1. Phase composition of an electrochemical system. The filled circles indicate the localization of possible potential differences:
M_1 and M_2—electrode metals; L_1 and L_2—solutions; V—gas phase

the different phases. The energy state of the charged particle is therefore characterized in a general case by the sum of the chemical potential and its electrical energy in a given phase:

$$\mu_{ech} = \mu \pm zFg \tag{9.1}$$

The quantity μ_{ech} is called the *electrochemical potential*, and g corresponds to the potential difference between a point inside the material phase and a point at an infinite distance in vacuum. The equilibrium condition for charged particles in a two-phase system with phases *1* and *2* will be the equality of their electrochemical potentials

$$\mu_{ech_1} = \mu_{ech_2} \tag{9.2}$$

The work of transporting a unit charge from phase *1* to phase *2* is equal to the difference of its electrochemical potentials in these phases:

$$\mu_{ech_1} - \mu_{ech_2} = \mu_1 - \mu_2 \pm (zFg_1 - zFg_2) \tag{9.3}$$

Under equilibrium conditions, according to Eq. (9.2), this work is equal to zero.

Since in a real process of transport of a unit charge from one phase to the other chemical and electrical work is done simultaneously, it is only possible to determine the total energy effect corresponding

to the change of the electrochemical potential, but not its constituent parts. For this reason the absolute difference of electrical potentials (or the potential drop between two different phases) has not yet been measured experimentally. By contrast, the emf of an electrochemical system, or cell, E is readily measurable since it corresponds to the potential difference between two points within the same phase—say, points b and q within the same metal or a and r in a vacuum near the metal surface (Fig. 9.1). Figure 9.1 shows an open-circuit electrochemical cell with two pieces of the same metal at both ends. If the emf is considered positive, a positive current must flow along the path $M_2 \rightarrow M_1 \rightarrow L_1 \rightarrow L_2 \rightarrow M_2$, i.e., in the counterclockwise direction. The emf of the cell is equal to the sum of all the potential differences arising along the entire path of current flow. These potential differences may arise across boundaries between any two phases; in the case under consideration they will be localized between the points a and b, c and d, e and f, l and m, n and p, and q and r.

Before plunging into a discussion of the nature of these potential differences it is necessary to introduce the concepts used in electrochemical literature today.

The surface potential χ is defined as a potential representing the work required to carry a unit positive charge from the interior of the phase to a point in vacuum situated in the immediate vicinity of the surface of the given phase. The phrase "in the immediate vicinity" should not be taken in the strict sense; it is usually quantified as the minimal distance from the surface of the given phase at which the so-called image forces cease to operate; this distance is approximately 10^{-4} cm. The *internal*, or *inner*, *potential* g is identified as a potential difference corresponding to the work done to bring a unit negative charge from infinity in vacuum into the bulk of the material phase. And, finally, the *external*, or *outer*, *potential* χ represents the work necessary to carry a unit negative charge from infinity to a point also in vacuum but situated in the immediate vicinity of the surface of the phase. In line with the definition, one can write for a phase

β:
$$g_\beta = \chi_\beta + \psi_\beta \tag{9.4}$$

The relations between all the above potentials can be conveniently represented by the following system of equation:

$$\mu_\beta^i + z_i F\chi_\beta + z_i F\psi_\beta = \mu_{ech\ (\beta)}^i \tag{9.5}$$

$$\mu_\beta^i + z_i F\chi_\beta = \alpha_\beta^i \tag{9.6}$$

$$\psi_\beta + \chi_\beta = g_\beta \tag{9.7}$$

$$\alpha_\beta^i + z_i F\psi_\beta = \mu_{ech\ (\beta)}^i \tag{9.8}$$

$$\mu_\beta^i + z_i F g_\beta = \mu_{ech\ (\beta)}^i \tag{9.9}$$

From Eqs. (9.5) to (9.9) it follows that the chemical μ, electrochemical μ_{ech}, and real α potentials (see below) have the dimensions of energy, eV, while the surface χ, external ψ, and internal g potentials are expressed in units of electrical potentials, V. In accordance with the system of equations given above, the definitions of potentials can be somewhat modified and explained. The electrochemical potential $\mu^i_{ech(\beta)}$ is the total energy of transfer of a charged species i from infinity to a point in the interior of the phase β. The chemical potential μ^i_β is the energy of interaction of a charged particle i in the bulk of the phase β with the particles forming that phase. The surface potential χ_β is defined as a measure of the change in the energy of the charged particle i on passing through the double dipole layer on the surface of phase β. The external potential ψ_β is a measure of the change in the energy of the charged particle i caused by its interaction with the free charge of phase β. The real and internal potentials are derivatives of μ and χ or ψ and χ, respectively, and their physical meaning is clear from Eqs. (9.6) and (9.7).

The potential differences between the points a and b, and q and r should be ascribed to the surface potentials between metal M and vacuum V; they may be designated, respectively, as χ_{VM_2} and χ_{M_2V}; naturally

$$\chi_{VM_2} = -\chi_{M_2V}$$

The potential difference between the points c and d inside the metallic phases M_2 and M_1 is the difference of the corresponding internal potentials, $g_{M_2M_1}$. The points e—f and n—p are the sites where the differences of internal potentials metal-solution (M_1-L_1) and solution-metal (L_2-M_2) are localized. These potential differences should be denoted, respectively, by $g_{M_1L_1}$ and $g_{L_2M_2}$. The difference of internal potentials is called the *Galvani potential*; g_{LM} potentials are often called *Nernst potentials* and designated by ε, like the electrode potential, though actually their physical meaning is different. The difference in the external potentials of the phases α and β is called the *Volta potential* $\psi_{\alpha\beta}$. For example, the potential difference between the points a and B is the Volta potential across the boundary between the metals M_1 and M_2, i.e., the quantity $\psi_{M_1M_2}$, and the potential difference between the points B and C is the Volta potential, $\psi_{M_1L_1}$, across the metal-solution (M_1-L_1) interface.

Finally, the potential difference between the points l and m is the Galvani potential across the solution-solution (L_1-L_2) interface and the symbol used is $g_{L_1L_2}$. Here two cases should be distinguished. If the solutions L_1 and L_2 correspond to two different immiscible solvents, then $g_{L_1L_2}$ is the Galvani potential between two liquids or the liquid junction potential. But if the solutions L_1 and L_2 differ from each other in the nature or concentration of the electro-

lyte, and not in the nature of the solvent, the potential is known as the *diffusion potential*; it is designated ψ_d.

Thus, the emf of an electrochemical system, or cell, is the sum of the following potential differences:

$$E = \chi_{vM_2} + g_{M_2M_1} + g_{M_1L_1} + g_{L_1L_2} + g_{L_2M_2} + \chi_{M_2v} \qquad (9.10)$$

or, after the terms equal in magnitude but opposite in sign are cancelled out,

$$E = g_{M_2M_1} + g_{M_1L_1} + g_{L_1L_2} + g_{L_2M_2} \qquad (9.11)$$

Hence, the emf of an electrochemical cell is composed of the following four potential differences: the Galvani potential between two metals, two Nernst potentials, and the Galvani potential between two solutions. In many electrochemical systems the liquid junction potential $g_{L_1L_2}$ is either absent or may be reduced to a minimum. So it is not an inevitable consequence of the nature of an electrochemical system and necessary component of its emf. The emf is therefore usually expressed as the sum of three potential differences:

$$E = g_{M_2M_1} + g_{LM_2} + g_{LM_1} \qquad (9.12)$$

In modern electrochemistry, the electrode potential ε is identified with the emf of a cell in which the electrode on the left is an SHE (standard hydrogen electrode), whose potential is conventionally taken as zero, and that on the right, the electrode whose potential is to be determined. In our case the left-hand electrode (or metal *1*) is platinum. The emf of the cell (as well as the electrode potential of metal *2*) is expressed as

$$\varepsilon_{M_2^{z+}/M_2} = g_{M_2Pt(H_2)} + g_{LM_2} - g_{LPt(H_2)} \qquad (9.13)$$

Thus, the electrode potential ε (just as the emf E) consists of three potential differences and includes the Galvani potential across the boundary between the electrode metal *2* and the platinum.

The emf of the cell is the difference of the potentials of the left-hand (M_2) and right-hand (M_1) electrodes, i. e.,

$$E = \varepsilon_r - \varepsilon_l$$

or, taking into account Eq. (9.13),

$$E = \varepsilon_r - \varepsilon_l = g_{M_2M_1} + g_{LM_2} - g_{LM_1} \qquad (9.14)$$

since

$$g_{M_2Pt} - g_{M_1Pt} = g_{M_2M_1}$$

Equations (7.17) and (9.12) provide two different ways for expressing the emf, and show that the cell emf, being the difference of two electrode potentials, is at the same time a sum of three Galvani potentials.

9.1.2. ELECTROMOTIVE FORCE AND ELECTRODE POTENTIAL AS THE SUMS OF VOLTA POTENTIALS

The consideration of single potential differences in electrochemical systems leads to the conclusion that electrode potentials are not identical in their physical nature. The electrode potentials of redox reactions described by the scheme

$$\text{Red, Ox/Pt}$$

do not include the contact potential difference between two metals and are therefore simpler than, say, the potentials of electrodes of the first kind

$$M^{z+}/M$$

which inevitably contain the Galvani potential g_{PtM}. The potentials of gas electrodes are also determined solely by Nernst potential differences, while those of electrodes of the second kind are composed of contact as well as Nernst potentials.

The nature of the single potential differences across the interfaces of electrochemical systems, or their number, may serve as the basis for their classification. Either classification (i.e., either that based on the nature of the process and the form of the emf equation or that based on the number of potential differences constituting the emf) yields approximately the same distribution of cells between the various types. For example, complex (double) chemical cells involve the largest number of single potential differences, while the emf of a concentration gas cell is composed of two Nernst potentials.

The breakdown of the emf into single potential differences yields additional information on the nature of electrochemical systems. But the basic equation (9.12) connecting the emf with potential differences cannot be considered satisfactory. The actually measurable emf is expressed here as the sum of Galvani potentials, each between two points in different phases and therefore inaccessible to direct measurement or determination. For equilibrium electrochemical systems this uncertainty can be eliminated if one takes into account that the change in the energy of a system in reversible processes is determined by its final and initial states and is independent of the mode of transition from one state to the other. In view of this the direct contact between the phases constituting an electrochemical system (see Fig. 9.1) may be replaced by contact through a vacuum (Fig. 9.2). As seen from Fig. 9.2, which contains only one solution L, the emf of the system should be written as the sum

$$E = \chi_{V2} + \chi_{2V} + \psi_{21} + \chi_{V1} + \chi_{1V} + \psi_{1L} + \chi_{VL} + \chi_{LV} + \psi_{L2} + \chi_{V2} + \chi_{2V} \qquad (9.15)$$

Taking into account that for any potential difference an equation of the type

$$\psi_{\alpha\beta} = -\psi_{\beta\alpha}$$

holds good, we get[1], in place of Eq. (9.15),

$$E = \psi_{21} + \psi_{L2} - \psi_{L1} \tag{9.16}$$

The emf of the system is now composed of three Volta potentials, each of which, like the emf itself, is a directly measurable quantity;

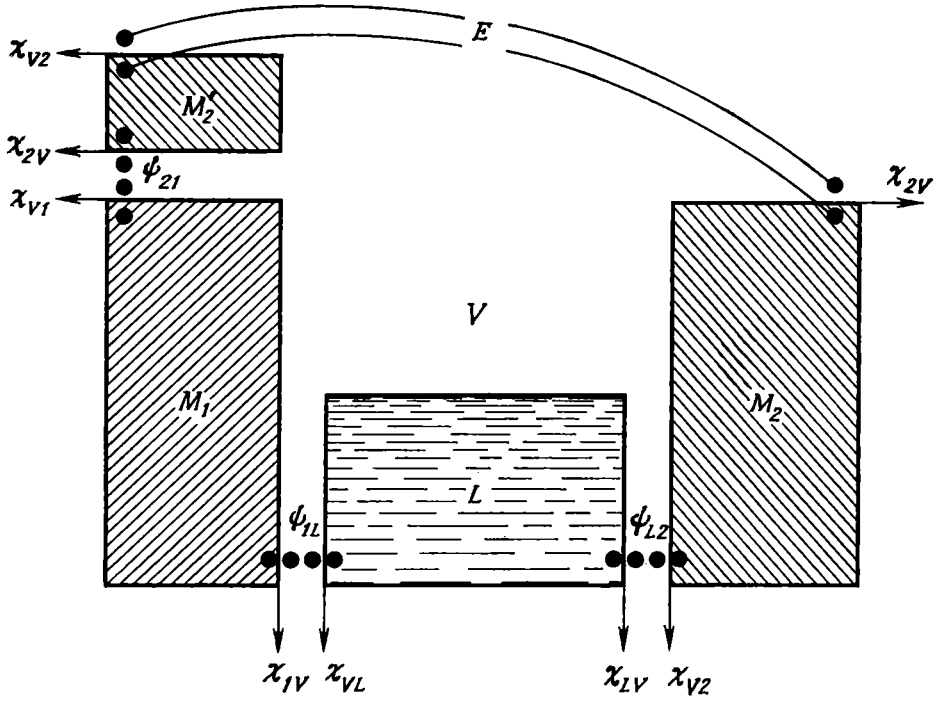


Fig. 9.2. The emf of an electrochemical system as a sum of Volta potentia l

they all represent the electrical work done to transport a unit charge between the corresponding points within the same phase. Equation (9.16) can also be obtained from the arrangement shown in Fig. 9.1 if a unit charge is carried along the path *aBCDr* and the solutions L_1 and L_2 are assumed to be identical, i.e., $\psi_{CD} = \psi_{L_1L_2} = 0$. The electrode potential on the arbitrary hydrogen scale can also be expressed by Eq. (9.16) provided that metal *1* is taken to mean platinum saturated with hydrogen at atmospheric pressure and dipped into a solution with a hydrogen ion activity $a_{H^+} = 1$ and the quantity ψ_{L_1} is the Volta potential corresponding to the hydrogen electrode.

[1] The bringing of two phases into direct contact changes the values of corresponding surface potentials, but this does not invalidate Eq. (9.16).

It should be stressed that the experimentally accessible emf corresponds to the difference of inner potentials of points in two pieces of the same metal connected to the electrodes of an electrochemical cell (the points b and q in M_2 and M_2', respectively in Fig. 9.1):

$$E = g_b - g_q = g_{M_2} - g_{M_2'} \tag{9.17}$$

As noted earlier, the difference of inner potentials cannot be determined in a general case, but since M_2 and M_2' are of the same chemical composition, their chemical potentials are equal, i.e., $\mu_{M_2} = \mu_{M_2'}$, and Eq. (9.17) may be replaced by

$$E = g_{M_2} - g_{M_2'} + \frac{\mu_{M_2}}{F} - \frac{\mu_{M_2'}}{F} = \frac{1}{F}(\mu_{ech(M_2)} - \mu_{ech(M_2')}) \tag{9.18}$$

According to Eq. (9.18), the emf is the difference of the electrochemical potentials of an elementary charged particle in M_2 and M_2', i.e., a directly measurable quantity. For the case under examination $\chi_{M_2} = \chi_{M_2'}$ and

$$E = g_{M_2} - g_{M_2'} = \psi_{M_2} + \chi_{M_2} - (\psi_{M_2'} + \chi_{M_2'}) = \\ = \psi_{M_2} - \psi_{M_2'} \tag{9.19}$$

that is, the emf is equal to the difference of external potentials near two metallic phases of the same chemical composition (the points a and r in Fig. 9.1), which can also be measured.

Thus, the emf of an open-circuit electrochemical cell is given by the equation

$$E = g_{M_2M_2'} = \psi_{M_2M_2'} = \frac{1}{F}(\mu_{ech(M_2)} - \mu_{ech(M_2')}) \tag{9.20}$$

Equation (9.20) is valid also for an electrochemical cell which is not at equilibrium, provided that the surface and chemical potentials of the phase are independent of its free charge.

9.1.3. THE PHYSICAL AND CHEMICAL THEORIES OF THE ORIGIN OF ELECTROMOTIVE FORCE IN ELECTROCHEMICAL SYSTEMS

The magnitude of electrode potential does not in general coincide with the Nernst potential, nor with the difference in the Nernst potentials of a metal and electrode H^+/H_2, Pt since it includes also the contact potential between the given metal and the platinum. For this reason the concept of electrode potential is more complicated than the concept of the potential difference across an electrode-solution interface and cannot be reduced to it. The so-called physical theory of electrochemical systems formulated by Volta at the beginning of last century placed special emphasis on the contact between

two dissimilar metals. According to this theory, the emf of an electrochemical system is taken as equal to the Volta potential between two dissimilar metals, and the Volta potential difference across a metal-solution interface as equal to zero. The generation of a current

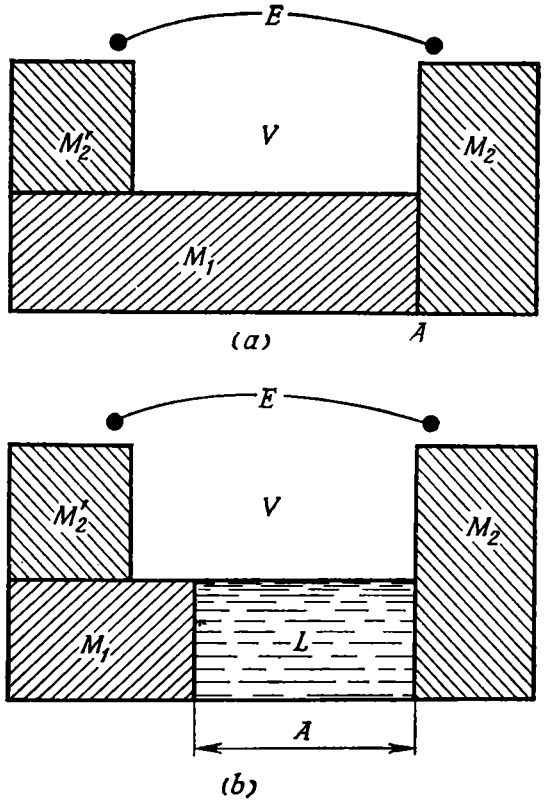


Fig. 9.3. Schematization of the physical theory of the generation of emf upon transition from a system consisting of two metals (*a*) to a system consisting of the same metals with an added separating solution layer (*b*)

in an electrochemical cell is explained as follows. If two dissimilar metals are brought into direct contact (Fig. 9.3*a*), no emf will be formed since

$$E = \psi_{M_2} - \psi_{M_2'} = \psi_{M_2'M_1} + \psi_{M_1M_2} = \psi_{M_2'M_1} - \psi_{M_2M_1} = 0$$

But if direct contact between the two metals at the boundary A is replaced by contact through a current-conducting solution (see Fig. 9.3*b*), the emf of the cell will be equal to $\psi_{M_2M_1}$:

$$E = \psi_{M_2} - \psi_{M_2'} = \psi_{M_2'M_1} + \psi_{M_1L} + \psi_{LM_2} = \psi_{M_2'M} = \psi_{M_2M_1}$$

since

$$\psi_{M_1L} = 0 \text{ and } \psi_{LM_2} = 0$$

As a result, an electric current will flow through the cell, i.e., the cell will produce electrical energy.

The Volta theory ignores the Nernst potential difference and thus cannot account for the dependence of the emf on the electrolyte concentration. Besides, it contradicts the basic law of thermodynamics—the law of conservation of energy—by postulating that energy arises out of the mere existence of an invariant potential difference between two metals, that is, out of nothing. The physical theory of Volta was critisized soon after it was created. In 1805 Ritter advanced his views, which were later developed by other scientists into the chemical theory of electromotive force. According to this theory, which was most thoroughly elaborated in the works of Nernst and Ostwald, in electrochemical systems electrical energy is produced by the chemical reactions taking place at the electrode-electrolyte interface. The chemical theory thus provides a correct definition of the source of electricity in electrochemical systems. It forms the basis of the quantitative thermodynamic expressions for electromotive force and electrode potentials considered earlier. Following this theory, Pisarzhevsky established a distinction between chemical and electrochemical processes and formulated a set of conditions necessary for chemical energy to be converted to electrical energy. At the same time the chemical theory assumes that the emf of an electrochemical system is only composed of two potential differences across the interfaces at which current-producing chemical reactions occur, i.e., across electrode-electrolyte interfaces. It neglects the contribution of the potential difference at the metal-metal junction to the emf. Electrode potentials are identified with potential differences across the electrode-solution interface, and the emf is given by

$$E = g_{LM_2} - g_{LM_1} \tag{9.21}$$

Now we know that these conceptions of the chemical theory are not true, and that in fact the emf of an electrochemical system consists of three potential differences.

The relation existing between electromotive force and single potential differences can be illustrated by considering, as an example, an electrochemical system consisting of two metals immersed in solutions of their current-conducting compounds:

$$M_2', \ M_1/M_1A//M_2A/M_2$$

The emf of the cell is determined by Eq. (9.16):

$$E = \psi_{M_2M_1} + \psi_{LM_2} - \psi_{LM_1}$$

since the diffusion potential at the boundary between the two solutions has been eliminated. If the potential differences ψ_{LM_1} and ψ_{LM_2} are eliminated by some means (say, by selecting solutions M_1A and M_2A of suitable composition), then, contrary to the conceptions of the chemical theory, the emf of the cell will be equal to the Volta

potential at the metal-metal interface, and not to zero[1]):

$$E = \varepsilon_r - \varepsilon_l = \psi_{M_2M_1} \tag{9.22}$$

Equation (9.22) underlies the parallelism discovered by Langmuir in 1917 between the emf of chemical cells and the contact potential difference across the metal-metal interface in these cells. If the composition of solutions M_1A and M_2A is altered, two additional potential differences, ψ_{LM_1} and ψ_{LM_2}, will appear, contributing to the emf in accordance with Eq. (9.16).

There are, however, electrochemical systems, say, a simple chemical cell with gas electrodes

$$Pt,\ H_2/H_2O/O_2,\ Pt$$

in which there is no contact between the two dissimilar metals, and hence, the contact potential $g_{M_2M_1}$ makes no contribution to the emf. The emf of such systems is given by Eq. (9.21), which follows from the chemical theory. The presence of a contact potential between the two different metals is not thus a prerequisite for the appearance of an emf and the production of energy in electrochemical systems. Contrary to the conceptions of the physical theory, electrical energy can be obtained from an electrochemical cell with electrodes made of the same metal.

9.1.4. THE NATURE OF POTENTIAL DIFFERENCES ACROSS PHASE BOUNDARIES

A potential difference across an interface between two phases is produced by various factors, largely depending on the nature of the contiguous phases. One of the more general causes is an exchange of charges. At the moment the two phases are brought into contact, charges start leaking across the interface predominantly in one direction, this resulting in an excess of charge of a given sign on one side of the interface and a deficiency of them on the other. Such an uncompensated exchange results in the formation of an electrical double layer and hence gives rise to a potential difference. The latter will in turn influence the kinetics of charge exchange, tending to level out the rates of transfer of charged particles in both directions. As the potential difference increases there will come a moment when no preferred transfer of charged particles from one phase to the other will occur and their velocities in both directions will become equal. This value of potential difference corresponds to an equilibrium between the phases at which the electrochemical potentials of the charged

[1]) Electrode potentials corresponding to such experimentally realizable conditions were named by A. Frumkin *potentials of zero charge*; he noted that the actual relations are more complicated and Eq. (9.22) is only approximate.

particles in the two phases are equal. Both positive and negative ions and also electrons may be involved in the charge exchange between the two phases. Which of these particles go from one phase to the other and are thus responsible for the appearance of a potential difference depends on the nature of the contiguous phases. For interfaces between a metal and a vacuum or between two different metals electrons usually play the role of such particles. With an interface between a metal and a solution of its salt the cations of the metal take part in the exchange. A potential difference across the interface between glass and a solution or between an ion-exchange resin and

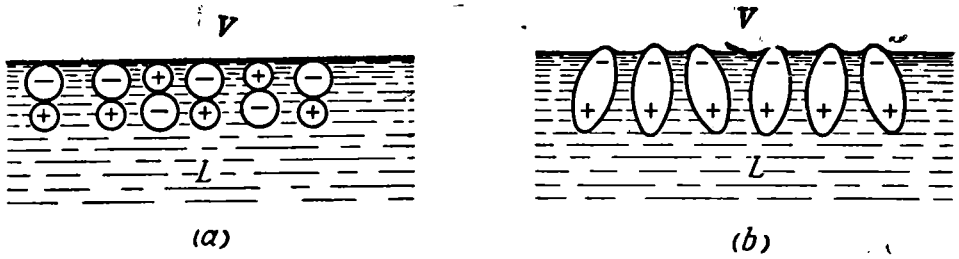


Fig. 9.4. Development of a potential difference at a vacuum-liquid interface as a result of (*a*) selective adsorption of ions, and (*b*) oriented adsorption of polar molecules

a solution arises from an exchange involving two species of like-charged ions. The particles exchanged at a glass-solution interface or at the boundary between a cation-exchange resin and a solution are ions of an alkali metal and hydrogen; for interfaces between an anion-exchange resin and a solution it is a hydroxyl ion and some other anion. When two immiscible liquids in which one and the same electrolyte is dissolved are brought into contact, a potential difference develops as a result of a nonequivalent transfer of oppositely charged ions of the electrolyte from the one phase to the other, as with the diffusion potential. Thus, neither the liquid-junction nor the diffusion potential is an equilibrium potential.

Another cause responsible for the development of potentials is the preferred (selective) adsorption of ions of one sign near the phase boundary. In this case one of the phases is impermeable to ions, and the potential difference is localized not on both sides of the interface (as with the exchange mechanism of formation of a potential difference) but inside one of the phases, in the immediate vicinity of the interface (Fig. 9.4*a*). A typical example of potential formed by this mechanism is the potential at a solution-gas interface. The absolute value of this potential difference cannot be measured, but one can trace its variation with composition of the solution, though this involves considerable experimental difficulties. Such measurements were carried out by Gouy, Quincke, and also by Frumkin and coworkers. It has been found that the strongest tendency

towards selective adsorption is usually displayed by anions. Therefore, the negative charge sheet of the double layer formed is often, though not always, situated closer to the interface and the positive sheet, away from it, in the bulk of the solution.

A third possible factor responsible for the appearance of a potential difference is associated with the tendency of polar uncharged particles towards oriented adsorption near the boundary between two phases. In oriented adsorption one of the ends of the dipole of a polar molecule faces the interface and the other, the phase to which the given molecule belongs (Fig. 9.4*b*). The value of the potential depends on the number of adsorbed molecules, their dipole moment and degree of orientation. If only one of the two contiguous phases is polar, a double layer will form on that side of the interface within the given phase; no potential difference will develop in the other, nonpolar phase. But if both phases are polar, an electrical double layer and the corresponding potential difference will appear in each phase near the phase boundary.

The role of polar particles (the oriented adsorption of which gives rise to a potential) can be played by molecules of both solute and solvent provided they are capable of being selectively adsorbed at the phase boundary. As the concentration of these substances increases, the potential difference is observed to increase gradually up to a certain limiting value, which will no longer change upon further addition of a surface-active substance. This limiting value corresponds to the saturation of the surface layer with polar molecules.

The development of a potential difference across the phase boundary cannot be attributed, in a general case, to any one of the factors quoted above; it arises, as a rule, from the combined effect of several parallel processes. The Galvani potential between two phases α and β may therefore be represented, following Lange, as the sum of three potentials:

$$g_{\alpha\beta} = g_q + g_s + g_{dip} \tag{9.23}$$

where g_q = potential due to the transfer of charged particles from the one phase to the other

g_s = potential arising from specific (or contact) adsorption of ions

g_{dip} = dipole potential resulting from oriented adsorption of polar molecules at the phase boundary.

From Eq. (9.23) it follows that if there is no exchange of charged particles, there remains a potential difference associated with adsorption of ions and dipoles:

$$g_{\alpha\beta} = g_s + g_{dip} \tag{9.24}$$

And if, in addition, specific (or contact) adsorption of ions is excluded, there will still remain the potential difference arising from oriented

adsorption of polar molecules:

$$g_{\alpha\beta} = g_{dip} \tag{9.25}$$

Only in the absence of all the three effects (or in the case of their mutual compensation) will the potential difference between the two phases be equal to zero.

9.2. THE THEORY OF FORMATION OF ELECTRODE POTENTIALS

An electrode potential is a very complex quantity composed of three single potential differences: the potential difference at the electrode metal-platinum interface, and the metal-solution and platinum-solution potential differences. The theory of development of electrode potentials must therefore be based on definite conceptions of the nature of both the contact potential between the two metals and the potential difference across the metal-solution interface.

9.2.1. THE CONTACT POTENTIAL AT THE BOUNDARY BETWEEN TWO METALS

The relation existing between the Volta and Galvani potentials can be found by using the rule, according to which the sum of all the works of transferring a unit charge along a closed path is zero. Hence, the total work necessary to transfer an electron across two contiguous metals in vacuum along the path indicated in Fig. 9.5 must also be equal to zero, i.e.,

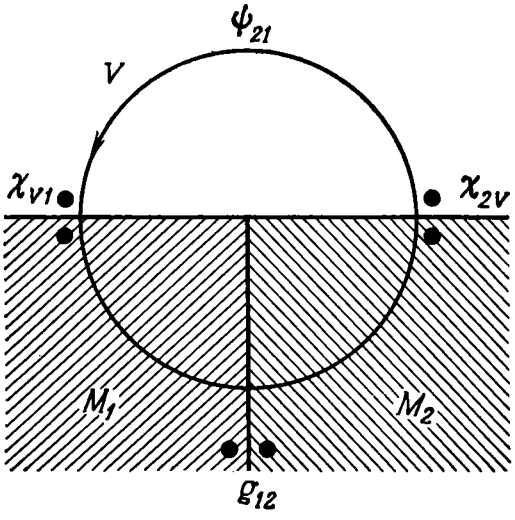


Fig. 9.5. Relation between the Volta and Galvani potentials

$$\chi_{V1} + g_{12} + \chi_{2V} + \psi_{21} = 0$$

or

$$g_{12} = \psi_{12} + \chi_{1V} + \chi_{V2} \tag{9.26}$$

according to Eq. (9.4), which is applicable to two phases.

Thus, the Galvani potential between two phases is equal to the Volta potential plus the sum of the two surface potential differences. Equation (9.26) may be regarded as the generalized form of Eq. (9.4) for a single phase.

The work necessary to bring a particle i of charge zF from one phase to the other is known to be defined by the difference of the ele-

ctrochemical potentials of that charged particle in two phases, for example, by the difference $\mu^i_{ech_1} - \mu^i_{ech_2}$ for the phases 1 and 2 (Fig. 9.5).

Using Eq. (9.9.), one can write:

$$\mu^i_{ech_1} - \mu^i_{ech_2} = \mu^i_1 - \mu^i_2 + z_i F g_{12} \tag{9.27}$$

where μ^i_1 and μ^i_2 = chemical potentials of particle i in phases *1* and *2*
g_{12} = Galvani potential at the boundary between these phases.

Substituting the value of g_{12} from Eq. (9.26) into Eq. (9.27), one has

$$\mu^i_{ech_1} - \mu^i_{ech_2} = \mu^i_1 - \mu^i_2 + z_i F \chi_{1V} - z_i F \chi_{2V} + z_i F \psi_{12} \tag{9.28}$$

For the boundary between each of these phases, j, and vacuum, the following equation holds:

$$\mu^i_{ech_j} = \mu^i_j + z_i F \chi_j + z_i F \psi_j \tag{9.29}$$

The electrochemical potential of a particle i in phase j as well as its external potential ψ_j can be measured experimentally. The difference of these potentials, which is equal to the sum of the chemical and surface potentials

$$\mu^i_{ech_j} - z_i F \psi_j = \mu^i_j + z_i F \chi_j \tag{9.30}$$

can also be measured. The quantity $\mu^i_j + z_i F \chi_j$ is known as the real potential α^i_j of a particle i in phase j:

$$\mu^i_j + z_i F \chi_j = \alpha^i_j \tag{9.31}$$

The real potential is equal in magnitude and opposite in sign to the work done to carry a particle i from a phase j into vacuum, to a point in the immediate neighbourhood of the surface of the phase j. This work is called the *work function* (or *exit work*) of the particle i and is denoted by the letter ω

$$\omega^i_j = -\alpha^i_j \tag{9.32}$$

Substituting the values of the work function from Eq. (9.32) into Eqs. (9.28) and (9.29) gives, respectively,

$$\mu^i_{ech_1} - \mu^i_{ech_2} = \omega^i_2 - \omega^i_1 + z_i F \psi_{12} \tag{9.33}$$

and

$$\mu^i_{ech_j} = -\omega^i_j + z_i F \psi_j \tag{9.34}$$

Equation (9.27) permits one to obtain the value of the Galvani potential between two phases *1* and *2* in equilibrium. At equilibrium

$$\mu^i_{ech_1} - \mu^i_{ech_2} = 0$$

and

$$g_{12} = \frac{\mu_2^i - \mu_1^i}{z_i F} \tag{9.35}$$

If both phases are metals, electrons with a charge of $z_i F = -e$ will be exchanged between them. In this case Eq. (9.35) must be rewritten in the form

$$g_{12} = \frac{\mu_1^e - \mu_2^e}{e} \tag{9.36}$$

that is, the Galvani potential at the junction between two contiguous metals is determined by the difference of the chemical potentials of the electrons in these metals. Equation (9.36) could be used as a basis for calculating the Galvani potential if the chemical potentials of the electrons in the two phases were known. However, as noted above, the variation of the chemical potentials alone cannot be determined for charged particles because during their transport from one phase to the other electrical work is performed as well as chemical. Equations (9.35) and (9.36) thus provide only the relation between the chemical potentials and the Galvani potential but do not enable the latter to be calculated.

Combining Eqs. (9.32) and (9.33), one obtains the following expression for the Volta potential between two phases *1* and *2*:

$$\psi_{12} = \frac{\omega_1^i - \omega_2^i}{z_i F} \tag{9.37}$$

For the special case of contact between two metals one has

$$\psi_{12} = \frac{\omega_2^e - \omega_1^e}{e} \tag{9.38}$$

Thus, the Volta potential between two metals is equal to the negative difference between the work functions of an electron from the first and the second metal divided by the charge of the electron. The work function is a directly measurable quantity, and therefore the value of the Volta potential can be calculated with the aid of Eq. (9.38). The work function can be found, for example, from the temperature variation of a thermionic current by using the Richardson equation

$$i = AT^2 e^{-\frac{\omega^e}{kT}} \tag{9.39}$$

where A is the Richardson constant. The smaller the amount of work required to remove an electron from a metal, the larger the number of electrons that can leave the metal at a given temperature and enter vacuum and the greater will be the excess positive charge in the metal. When two metals with different work functions are brought close together, the electrons will jump out of the metal with the smaller work function and rush to the one with the larger work func-

tion. As a result, the first metal will be charged positively and the second, negatively, as follows from Eq. (9.38).

The most probable values of work functions for different metals are shown in Table 9.1. The values of work functions enable one to calculate the ψ_{12} potentials for different metals. For example, for the pair Cu/Zn

$$\psi_{Cu/Zn} = \frac{1}{e}(\omega_{Cu} - \omega_{Zn}) = \psi = 0.3 \text{ V}$$

while the emf of the cell

$$Zn/ZnSO_4 \mid CuSO_4/Cu$$

is 1.11 V. Thus, the ψ_{12} potential constitutes an appreciable part of the reversible emf of the electrochemical cell. Data on work functions are not very accurate, but as the experimental technique is improved the disparity between the values of work functions obtained by different authors is reduced to a minimum. For most metals the experimental data depart from the average value by not more than $\pm$ 0.2 eV, more frequently by $\pm$ 0.1 eV; for this reason the values in Table 9.1 are given with an accuracy up to tenths of an electron-volt.

TABLE 9.1

Values for the Work Function of Some Metals

Metal	Work function, eV	Metal	Work function, eV
Ag	4.3	Mo	4.3
Al	4.3	Na	2.3
Bi	4.5	Ni	4.5
C (graphite)	4.7	Pb	4.0
Cd	4.0	Pt	4.9
Co	4.4	Sb	4.6
Cr	4.6	Sn	4.3
Cu	4.5	Ti	4.0
Fe	4.7 (4.35)	Tl	3.9
Ga	4.1	V	4.1
Hg	4.5	W	4.5
K	2.2	Zn	4.2
Mg	3.6	Zr	3.9
Mn	3.8		

9.2.2. THE NERNST OSMOTIC THEORY

The first quantitative theory of electrode potential was proposed by Nernst in 1890; it is called the *osmotic theory of electrode potential and electromotive force.* Nernst's theory played an important part

in the development of electrochemistry. The principles underlying this theory are as follows:

1. The electrode potential is determined by the metal-solution potential difference, while the emf of an electrochemical cell is the difference of two such single potential differences.
2. An electrode potential arises only from the exchange of ions between the metal and the solution.
3. The driving forces for ion exchange are the osmotic pressure of the solute and the electrolytic dissolution pressure of the metal.

The first principle cannot be regarded as correct since the potential difference across the metal-solution interface does not, in a general case, coincide with the electrode potential but is only a certain part of it. The assumption that the emf of an electrochemical cell is always equal to the difference of two Galvani potentials is also erroneous. The emf is composed not of two but of three potential differences, including the potential arising at the junction between two different metals. Thus, the Nernst theory cannot be looked upon as the theory of electrode potential and electromotive force. In fact it is the theory of the metal-solution Galvani potential, i.e., of that component of the electrode potential and emf which depends on the composition of the solution.

The second principle is a correct reflection of the mechanism of formation of an equilibrium potential difference across the metal-solution interface, although ion exchange is not the only possible cause of the appearance of a potential difference across that interface. If an equilibrium exists between the electrode and the solution, the magnitude of electrode potential will be a measure of the change of the Helmholtz free energy $\mathfrak{F}$ (or the Gibbs free energy G) of the corresponding electrode reaction. The electrode potential must be a definite and constant quantity for a given electrode reaction. From the equation for the electrode potential

$$\varepsilon_{LM} = g_{MPt} + g_{LM} - g_{LPt}$$

where g_{MPt} and g_{LPt} are constant quantities for the chosen metal, it follows that at equilibrium not only

$$\varepsilon_{LM} = \text{const}$$

but also

$$g_{LM} = \text{const}$$

that is, the metal-solution potential difference at equilibrium is governed by the nature of the electrode reaction and is not affected by the presence of surface-active substances. In other words, for the case under consideration

$$g_{LM} = g_q + g_s + g_{dip} = \text{const}$$

At the same time it should be taken into account that the presence of surface-active substances of the ionic or molecular type may affect all the three components (g_q, g_s, and g_{dip}) of the total potential difference, but the quantity g_{LM} remains unchanged.

Thus, the Nernst theory refers to only one component of the Galvani potential at the metal-solution interface, namely, to the quantity $g_{LM(q)}$, which is actually the Nernst potential in the proper sense.

The assumption of exchange between the metal and the solution during the formation of the equilibrium potential (and on reaching it) was confirmed by numerous investigations with tracer atoms carried out after Nernst proposed his theory. If we add to the electrode metal (it is most convenient to use metal amalgams for such experiments) a certain amount of its radioactive isotope and bring the electrode in contact with a solution of a salt of the same metal, the solution will also display radioactive properties after some time. A similar result will be obtained if we prepare a solution of a salt of the electrode metal containing its radioactive isotope and use an electrode made of a nonradioactive metal. Then the electrode also becomes radioactive after some time. This effect is possible only when there is ion exchange between the electrode and the solution.

The use of this and a number of other methods has made it possible not only to confirm the fact of ion exchange but also to estimate it quantitatively. Since exchange involves charged particles, the intensity of the process can be expressed in terms of current and is called the *exchange current* I^0 or exchange current density i^0 if referred to unit surface. Exchange current density is expressed in amperes per unit surface area (1 cm^2) of the electrode-solution interface; it serves as a kinetic characteristic of the equilibrium between the electrode and the solution at the equilibrium value of the electrode potential. One of the first studies devoted to the determination of exchange current densities was carried out by V. Royter and coworkers (1939). The values of exchange current density for some electrodes are given in Table 9.2. The exchange intensity depends on the nature of the electrode and of the electrolyte within wide limits.

According to the third principle of the Nernst osmotic theory exchange currents arise under the effect of the osmotic pressure of the solution and the electrolytic dissolution pressure of the metal.

Using these three principles, Nernst obtained a qualitative picture of the development of the metal-solution potential difference and deduced a quantitative relationship between the value of this potential difference and the composition of the solution. His reasoning was as follows.

At the instant of immersion of a metal in a solution of its own ions an exchange of ions begins between the metal and the solution. Three cases are possible, depending on the nature of the metal and on the composition of the solution (Fig. 9.6):

TABLE 9.2

Exchange Current Densities at Room Temperature for Some Electrodes

Electrode	Solution	Exchange current density, A/cm^2
H^+/H_2, Hg	$1.0N$ H_2SO_4	5×10^{-13}
Ni^{2+}/Ni	$2.0N$ $NiSO_4$	2×10^{-9}
Fe^{2+}/Fe	$2.0N$ $FeSO_4$	10^{-8}
Zn^{2+}/Zn	$2.0N$ $ZnSO_4$	2×10^{-5}
Cu^{2+}/Cu	$2.0N$ $CuSO_4$	2×10^{-5}
Zn^{2+}/Zn, Hg	$2\times10^{-3}N$ $Zn(NO_3)_2+1.0N$ KNO_3	7×10^{-4}
H^+/H_2, Pt	$0.2N$ H_2SO_4	1×10^{-3}
Na^+/Na, Hg	$1.0N$ $NaOH+1\times10^{-3}N$ $N(CH_3)_4OH$	4×10^{-2}
Pb^{2+}/Pb, Hg	$2\times10^{-3}N$ $Pb(NO_3)_2+1.0N$ KNO_3	10^{-1}
Hg^{2+}/Hg	$2\times10^{-3}N$ $Hg_2(NO_3)_2+2.0N$ $HClO_4$	5×10^{-1}

(1) the osmotic pressure π is higher than the electrolytic dissolution pressure P (Fig. 9.6*a*);

(2) the osmotic pressure π is lower than the electrolytic dissolution pressure P (Fig. 9.6*b*);

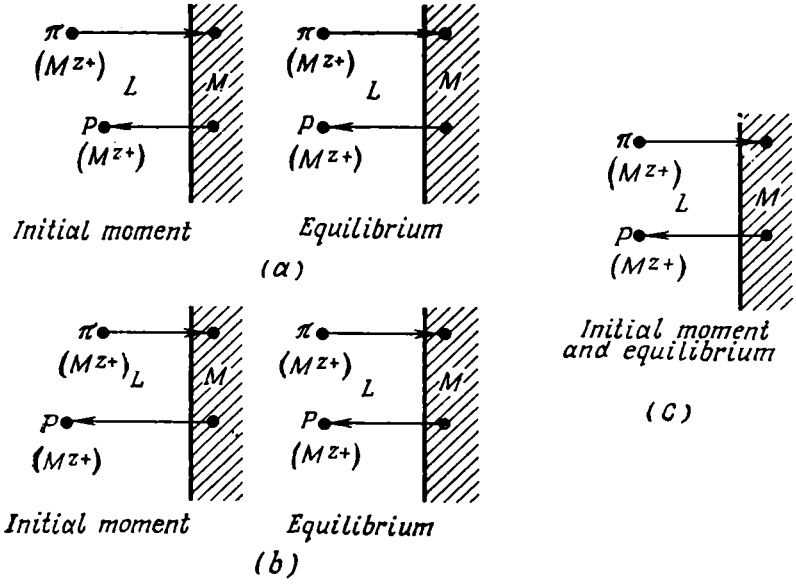


Fig. 9.6. Development of a potential difference at the metal-solution interface according to Nernst. The lengths of the arrows (in arbitrary units) are proportional to the rates of the corresponding processes

(3) the osmotic pressure π is equal to the electrolytic dissolution pressure P (Fig. 9.6*c*).

As soon as the metal and solution are brought into contact, there begins a predominant transfer of ions either from the solution into

the metal (case 1, at $\pi > P$) or vice versa (case 2, at $\pi < P$). Since the metallic ions are charged entities, their preferential transfer to any one of the phases will lead to the accumulation of an excess positive charge in this phase, while the other phase will be charged negatively. In either case the potential difference arising from the nonuniform charge distribution will have an accelerating effect on the slow reaction and put a brake on the fast reaction (see Fig. 9.5); this is typical of the exchange mechanism of development of an interphasial potential difference. After a certain (very short) period of time the potential difference will equalize the exchange rates in both directions. The potential will no longer change, retaining a constant value corresponding to the equilibrium between the metal and solution. In just the same way the rates of charge-transfer reactions in the directions solution-metal $\vec{I}$ and metal-solution $\overleftarrow{I}$ will become constant and equal in magnitude to the exchange current

$$\vec{I} = \overleftarrow{I} = I^0 \tag{9.40}$$

Under these conditions the osmotic work

$$RT \ln \frac{P}{\pi}$$

will be balanced by the electrical work

$$g_q zF$$

that is,

$$RT \ln \frac{P}{\pi} + g_q zF = 0 \tag{9.41}$$

whence

$$g_q = -\frac{RT}{zF} \ln \frac{P}{\pi} \tag{9.42}$$

Since in the osmotic theory the Galvani potential at the solution-metal interface is identified with the electrode potential, Eq. (9.42) may be replaced by

$$\varepsilon_{LM} = -\frac{RT}{zF} \ln \frac{P}{\pi} \tag{9.43}$$

Equation (9.43) shows that at $\pi > P$ the metal is charged positively and the solution negatively; the quantity g_q, and hence the electrode potential, will be positive. At $\pi < P$ a reverse charge-transfer reaction takes place and the quantities g_q and ε_{LM} will therefore be negative. And, finally, when $\pi = P$, the metal will be uncharged with respect to the solution, and no potential difference will develop across the metal-solution interface, i.e., g_q and ε_{LM} will be equal to zero.

The above conclusions, which follow from the Nernst theory, should be considered erroneous because the potential difference g_q is only part of the electrode potential ε_{LM}. With g_q equal to zero the quantity ε_{LM} may be different from zero and depends on the work function of a given metal. Besides, the potential difference g_{LM} may differ from zero even when the exchange mechanism does not result in the appearance of excess charge on either side of the interface. The potential difference under these conditions may be attributed to the orientation of polar molecules and the specific adsorption of ions [see Eq. (9.23)].

Following the Arrhenius theory, Nernst assumed that the ideal gas laws are applicable to electrolytic solutions. The osmotic pressure of an electrolytic solution may therefore be expressed in terms of the concentration of the corresponding ions:

$$\pi = RTc$$

whence, on the basis of Eq. (9.43), one has

$$\varepsilon_{LM} = -\frac{RT}{zF} \ln \frac{P}{RT} + \frac{RT}{zF} \ln c_{M^{z+}} \tag{9.44}$$

If the concentration $c_{M^{z+}}$ in Eq. (9.44) is equal to one gram-ion per litre, then

$$\underset{(c=1)}{\varepsilon_{LM}} = -\frac{RT}{zF} \ln \frac{P}{RT} \equiv \varepsilon^0_{LM} \tag{9.45}$$

where ε^0_{LM} is the normal potential. Introducing the value of the normal potential, one can write, in place of Eq. (9.44), the following expression:

$$\varepsilon_{LM} = \varepsilon^0_{LM} + \frac{RT}{zF} \ln c_{M^{z+}} \tag{9.46}$$

Equation (9.46) bears a certain superficial resemblance to the general thermodynamic equation for the electrode potential as applied to the special case of metallic electrodes of the first kind. The Nernst normal potential may be identified with the standard potential if the concentrations in Eq. (9.46) are replaced by activities

$$\varepsilon_{LM} = \varepsilon^0_{LM} + \frac{RT}{zF} \ln a_{M^{z+}} = \varepsilon^0_{LM} + \frac{RT}{zF} \ln c_{M^{z+}} f_{M^{z+}}$$

Equation (9.46) is known as the *Nernst equation for the electrode potential*; the same name is often given to Eqs. (9.43) and (9.44) as well as to the general equation (7.7).

According to the Nernst theory, the normal potential is a simple function of the electrolytic dissolution pressure of a metal. It could be calculated for various metals from the known values of P. But such a calculation is impossible in practice since the quantity P

is not directly measurable. It is however possible to establish, by using the known values of standard potentials, how the quantity P varies from one electrode metal to another. If, for example, the electrolytic dissolution pressure corresponding to the standard hydrogen electrode is taken equal to 1 atm, the electrolytic dissolution pressure of beryllium will be about 10^{43} atm, and that of copper, 10^{-20} atm. These values cannot naturally be accepted as the actual pressures, and thus the concept of the electrolytic dissolution pressure introduced by Nernst evidently implies some other characteristics of the electrode-solution system.

The Nernst equation is valid for electrodes of the first kind, and its sphere of relevance is restricted to electrodes of this type. It must however be noted that this limitation does not undermine the Nernst theory. For example, Peters (1898) showed that Nernst's basic conceptions can be used for deducing the equation for redox electrodes. Nernst's ideas were developed in the works of Butler (1924), who succeeded in deriving kinetically equations for various types of electrodes.

From the Nernst theory it follows that standard electrode potentials are independent of the nature of the solvent since the quantity P, which determines the normal or standard electrode potential, is not a function of the properties of the solvent but depends on the properties of the metal. However, neither experiment nor theoretical considerations support these conceptions, a circumstance that calls for a revision of the physical premises of Nernst's theory.

9.2.3. THE HYDRATION (SOLVATION) THEORY OF ELECTRODE POTENTIAL

The Nernst osmotic theory is incapable of disclosing the physical essence of the processes giving rise to a potential difference across the metal-solution interface since it is founded on Arrhenius' idealized conceptions of electrolytic dissociation. The major shortcoming of the Arrhenius theory is that the properties of electrolytic solutions are identified with those of ideal gas systems, i.e., the ion-ion and ion-solvent interactions are ignored. The same drawback is inherent in the Nernst theory. The theory of electrode potentials developed along the same path as did the theory of electrolytic solutions. Both the shortcomings and achievements of the latter theory have been reflected in the theory of electrode potentials. For example, the introduction of the concepts of activity coefficient (as a quantity associated with ionic interaction) and activity as the effective concentration, which was a big step forward in the development of the theory of solutions, made it possible to obtain, on the basis of the Nernst theory, the correct relationship between the electrode potential and the composition of the solution. Taking into account solute-solvent interac-

tions (insisted on by Mendeleyev) and, particularly, the possibility of formation of hydrated or solvated ions in solutions (A. Kablukov) was an important landmark in the development of the theory of electrolytic solutions. As a consequence, it became possible to find the cause of dissociation of electrolytes into ions. Ion solvation evidently also plays substantial role in the attainment of an equilibrium between electrode and solution.

The Pisarzhevsky-Izgaryshev Theory. The mechanism of development of an electrode potential based on solvation phenomena was first formulated by L. Pisarzhevsky (1912-14). He thought that two processes are of decisive importance in the formation of an electrode potential. The first is the ionization of the electrode metal, in which ions and free electrons appear:

$$M = M^{z+} + ze \tag{9.47}$$

Equation (9.47) does not contradict the present-day views on the nature of the metallic state, according to which the crystal lattice of a metal contains its ions in equilibrium with delocalized valency electrons; the latter form an electron gas and ensure metallic conduction. The second process is the interaction of solvent L with the metal ions M^{2+} present in the crystal lattice; this process may be represented thus

$$M^{z+} + xL = ML_x^{z+} \tag{9.48}$$

The overall reaction giving rise to a potential difference across the metal-solution interface should therefore be written in the following form

$$M + xL - ML_x^{z+} + ze \tag{9.49}$$

The equilibrium constant for this reaction is

$$K = \frac{[ML_x^{z+}]\,[e]^z}{[M]\,[L]^x} \tag{9.50}$$

Thus, according to Pisarzhevsky, the transfer of ions from the metal into the solution is not due to the physically obscure electrolytic dissolution pressure of the metal but is the result of its interaction with the solvent molecules. The electrolytic dissociation of electrolytes and the development of an electrode potential are thus based on the same process of ion solvation (or ion hydration in the case of aqueous solutions). Here, as follows from the reaction (9.49), not free but solvated ions are formed on dissolution; their properties depend on the nature of the solvent. For this reason, as distinct from the Nernst theory, the standard potential of a given electrode must change from solvent to solvent. This relationship was discovered and examined by many authors (Izgaryshev, Brodsky, Pleskov, Hartley, Izmailov, and others). It has been found that the change in the electrode potential from solvent to solvent is the greater, the smaller

the radius and the greater the charge of the ion taking part in the electrode reaction. According to Pleskov the least variation of potential is observed for cesium, rubidium and iodine electrodes, where univalent ions of considerable size participate in the establishment of electrode equilibrium. Conversely, these variations are especially pronounced for hydrogen ions and polyvalent cations of small size. Precisely this dependence of electrode potential on the nature of the solvent could be expected on the basis of Pisarzhevsky's conceptions of the role of solvation phenomena in the development of a metal-solution potential difference. For quantitative comparison of potentials in different solvents the cesium electrode is used as the standard null electrode since its potential depends least of all on the nature of the solvent.

Izmailov suggested using the absolute hydrogen scale for all solvents. He found the difference in the solvation heats of the hydrogen ion for a number of solvents and calculated the difference in the standard potentials of the hydrogen electrode for the solvents studied. The data obtained by Izmailov on the effect of the solvent on the potentials of some electrodes are presented in Table 9.3.

TABLE 9.3

Standard Electrode Potentials in Different Solvents (in increasing order of positive value of potential in aqueous solution)

Electrode	Solvent				
	H_2O	CH_3OH	C_2H_5OH	HCOOH	NH_3
Li^+/Li	−2.95	−2.90	−2.70	−2.96	−3.24
Rb^+/Rb	−2.93	—	—	−2.93	−2.93
Cs^+/Cs	−2.93	−2.95	—	−2.92	−2.95
K^+/K	−2.92	−2.72	−2.60	−2.85	−2.98
Na^+/Na	−2.71	−2.58	−2.43	−2.90	−2.85
Zn^{2+}/Zn	−0.76	−0.54	−0.39	−0.73	−1.53
Cd^{2+}/Cd	−0.40	−0.23	−0.13	−0.23	−1.20
H^+/H_2, Pt	−0.00	+0.20	+0.25	+0.52	+1.00
I^-/I_2, Pt	+0.54	+0.56	+0.55	—	+0.45
Ag^+/Ag	+0.80	+0.96	+1.00	+0.69	−0.18
Cl^-/Cl_2, Pt	+1.34	+1.32	+1.30	+1.51	+1.03

It can be seen from Table 9.3 that not only the electrode potential changes from solvent to solvent but in some cases (e.g. the electrodes I^-/I_2 and Ag^+/Ag in water and in liquid ammonia) even the order of arrangement of electrodes in the electrochemical series. If an electrochemical cell, or system, is constructed with identical electrodes in different solvents, then a considerable emf will result, provided

the liquid junction potentials are eliminated. For example, the initial emf of the cell

$$Pt,\ H_2/H^+,\ HCOOH//H^+,\ NH_3/H_2,\ Pt$$

will amount to 1.52 V. This value exceeds the emf of the Daniell-Jakobi cell consisting of copper and zinc, which are so electrochemically different. Thus, the effect of the nature of the solvent on the electrode potential is quite comparable with that of the nature of the metal.

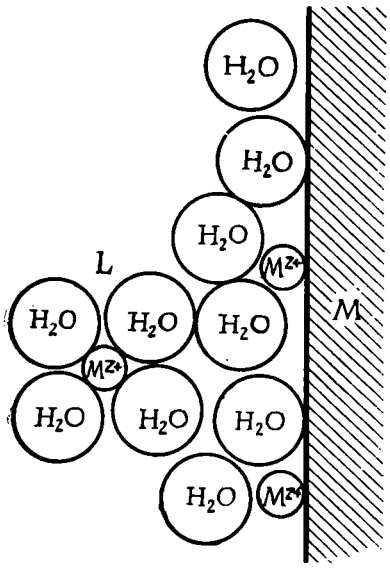


Fig. 9.7. Izgaryshev's model of the metal-solution interface during the formation of a potential difference

Of special interest in this connection are the works of Izgaryshev, who substantially developed (1926-28) Pisarzhevsky's qualitative conceptions and laid the foundation of the hydration (solvation) theory of electrode potentials and electromotive force. According to Izgaryshev, at the metal surface facing the solution one may find both metal ions and adsorbed water molecules (Fig. 9.7). The metal ions can pass from the aqueous into the metallic phase, losing their hydration sheath and taking their position in the crystal lattice. At the same time the molecules of water (or another solvent), being adsorbed and oriented in a definite way at the interface, can interact with the ions located in the metal and pull them out of its lattice under certain conditions. Thus, the electrode potential depends, according to Izgaryshev, on the strength of the ionic bond in the metal and on the ion hydration energy. Izgaryshev has also demonstrated how, on the basis of his theory, electrode potentials on the hydrogen scale and the emf's of various galvanic cells can be calculated from independent experimental data.

Further Development of the Solvation Theory of Electrode Potential. Conceptions similar to those forming the basis of the Pisarzhevsky-Izgaryshev hydration theory were later used by other authors. For example, in 1932 Gurney applied the kinetic method suggested by Butler to the problem of the development of the equilibrium electrode potential; Gurney's ideas concerning metal-solution interactions are consistent with Izgaryshev's theory. His calculations may therefore be regarded as a quantitative formulation of some of the basic propositions of Izgaryshev's hydration theory.

Following Gurney, we will assume that the probability of transfer of a metal ion from solution to electrode (in the forward direction)

is proportional to the number of metal ions in contact with the metal surface on the solution side of the interface (Fig. 9.7) and the probability of ion transfer in the opposite direction is proportional to the number of solvent molecules on the metal surface. Gurney assumed that for the number of forward $\vec{n}$ and reverse $\overleftarrow{n}$ transfers one can write

$$\vec{n} = \vec{k}N_m \tag{9.51}$$

and

$$\overleftarrow{n} = \overleftarrow{k}N_{\mathrm{L}} \tag{9.52}$$

where N_m = number of ions in the entire volume of solution
N_{L} = number of solvent molecules.

Since the energy levels of an ion in the solution and in the metal are different, the proportionality coefficients $\vec{k}$ and $\overleftarrow{k}$ must be functions of the energy change occurring when the ion is transferred from one

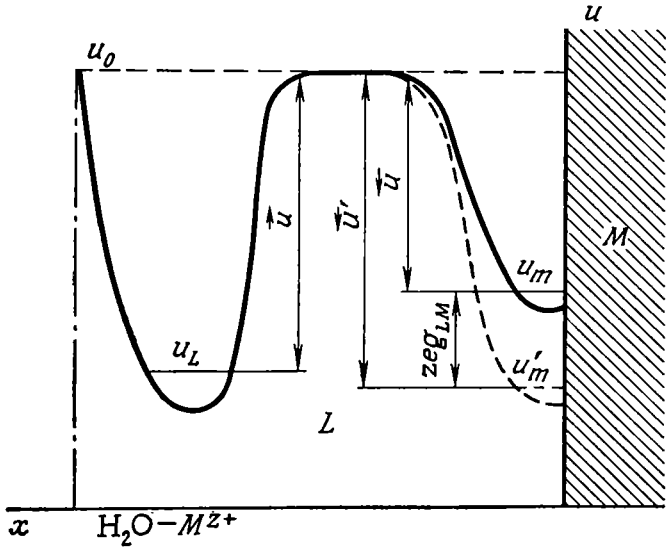


Fig. 9.8. Gurney's potential diagram

phase to the other. Such energy changes can be estimated with the aid of the diagram shown in Fig. 9.8. The left potential curve represents the change of the ion free energy as a function of the distance between the ion and the enveloping water molecules; the position of the water molecules is taken here as pre-assigned and is indicated by a dash-and-dot vertical line. The horizontal line u_{L} corresponds to the lowest vibration level of the ion in solution, and the u_0 line to the energy level of a free gaseous ion. The potential curve on the right shows the energy change for a metal ion as a function of its distance from the fixed metal surface. The horizontal line u_m corresponds to the lowest vibration level of the ion in the surface layer

of the metal lattice. For a forward transfer the ion must possess such an amount of energy $\vec{u}$ which would raise it from the u_L to the u_0 level. Then

$$\vec{u} = u_0 - u_L \tag{9.53}$$

The quantity $\vec{u}$ may be regarded as the energy required to remove the ion from the solution. An ion being transferred in the opposite direction must rise from the u_m to the u_0 level. Suppose that

$$\overleftarrow{u} = u_0 - u_m \tag{9.54}$$

Here $\overleftarrow{u}$ represents the energy required to bring the ion to the u_0 level; it may be defined as the work done to remove the ion from the metal. Assuming that the Maxwell-Boltzmann statistics is applicable to the ion distribution among energy levels, one can, in place of Eqs. (9.51) and (9.52), write equations taking into account changes in the energy of an ion in the course of forward and reverse reactions:

$$\vec{n} = \alpha N_m e^{-\frac{\vec{u}}{kT}} = \alpha N_m e^{\frac{u_L - u_0}{kT}} \tag{9.55}$$

and

$$\overleftarrow{n} = \beta N_L e^{-\frac{\overleftarrow{u}}{kT}} = \beta N_L e^{\frac{u_m - u_0}{kT}} \tag{9.56}$$

where α and β are the transfer probability factors.

Usually at the instant of immersion of a metal in a solution $\vec{n} \neq \overleftarrow{n}$, i.e., preferred transfer of ions in one direction is observed. As a consequence, a potential difference develops across the metal-solution interface, which in turn changes the energy states of the ions. When equilibrium is attained, the frequencies of ion transfers in both directions become equal:

$$\vec{n}_{(g_{LM})} = \overleftarrow{n}_{(g_{LM})}$$

where g_{LM} is the equilibrium potential difference between the metal and solution.

According to Gurney, the energy associated with the resulting potential will alter the energy state of the ions on the metal surface. In this case the u_m level drops down by the amount zeg_{LM} (to the u'_M level) as shown in Fig. 9.8 by a dotted curve. The number of back transfers will then be given by the equation

$$\overleftarrow{n}_{(g_{LM})} = \beta N_L e^{\frac{u_m + zeg_{LM} - u_0}{kT}} \tag{9.57}$$

Since $\vec{n}_{(g_{LM})} = \overleftarrow{n}_{(g_{LM})}$, it follows that

$$\alpha N_m e^{\frac{u_L - u_0}{kT}} = \beta N_L e^{\frac{u_m + zeg_{LM} - u_0}{kT}}$$

and

$$g_{LM} = \frac{u_L - u_m}{ze} + \frac{kT}{ze} \ln \frac{\alpha N_m}{\beta N_L} \tag{9.58}$$

Equation (9.58) relates the metal-solution potential difference to the ratio of the lowest vibration levels of a metal ion in the solution and metal and also to the concentration of the solution. The ratio of the number of solute particles to that of solvent molecules, N_m/N_L, may be taken as a quantity proportional to the concentration expressed, for example, in g-ion/litre. From Eqs. (9.53) and (9.54) and Fig. 9.8 it follows that

$$u_L - u_m = -(h - y) \tag{9.59}$$

where h represents the hydration energy of an individual ion in a solution of a given composition, and y corresponds to the work necessary to move the ion from the metal into vacuum, ω^i, taken with the minus sign. Using Eq. (9.59) and switching from ions to gram-ions, Gurney rewrites Eq. (9.58) in the following form:

$$g_{LM} = \frac{Y^i - \bar{U}_h}{zF} + \frac{RT}{zF} \log \gamma c \tag{9.60}$$

where $\gamma = \alpha k/\beta$ (k is a factor for conversion of N_m/N_L units expressing concentration to c units); $\bar{U}_h = N_A h$ and $Y^i = N_A y^i$. The hydration energy $\bar{U}_h$ refers to the ideal solution. In a real solution the hydration energy will be higher owing to ion-ion interactions [1]:

$$U_h > \bar{U}_h$$

The difference between the hydration energies U_h and $\bar{U}_h$ must depend on the concentration of the solution, i.e.,

$$U_h = \bar{U}_h + \varphi(c)$$

If we introduce a certain function of the concentration ξ given by the equation

$$RT \ln \xi = \varphi(c)$$

then

$$U_h = \bar{U}_h + RT \ln \xi \tag{9.61}$$

---

[1] For an ion to leave a real solution it must, apart from shedding its hydration sheath, overcome the attraction of the ionic cloud.

Substituting the value of $\bar{U}_h$ from Eq. (9.61) into Eq. (9.60) gives

$$g_{LM} = \frac{Y^i - U_h}{zF} + \frac{RT}{zF} \ln \xi c \tag{9.62}$$

The quantity ξ must correspond in its physical meaning to the activity coefficient f. Putting $\gamma = 1$ (which is highly probable) and assuming that $g_{LM} = \varepsilon_{LM}$ (which is incorrect), Gurney deduced the following equation for the electrode potential:

$$\varepsilon_{LM} = \frac{Y^i - U_h}{zF} + \frac{RT}{zF} \ln a_{M^{z+}} \tag{9.63}$$

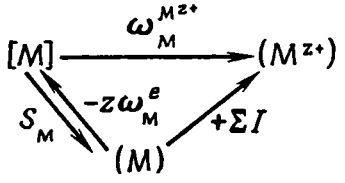
At $a_{M^{z+}} = 1$

$$\varepsilon_{LM} = \frac{Y^i - U_h}{zF} \equiv \varepsilon^0_{LM} \tag{9.64}$$

and the Gurney equation may be rewritten in the form

$$\varepsilon_{LM} = \varepsilon^0_{LM} + \frac{RT}{zF} \ln a_{M^{z+}}$$

As distinct from the Nernst equation which contains an uncertain quantity (the electrolytic dissolution pressure), Gurney's formula for the standard potential includes the work function of the ion and its energy of hydration, i.e., quantities possessing a definite physical meaning. The work function of the ion can be found with the aid of the following cycle:



The transfer of one gram-ion of a metal from the metal into vacuum requires an energy equal to the work function ω_M^{Mz+}. This transfer can also be effected in two steps. First, one gram-atom of the metal is converted to gaseous free atoms by sublimation, which requires the energy of sublimation S. Then, the gaseous metal atoms are ionized into gaseous ions of valency z. The energy used up at this stage is equal to the sum of ionization potentials, ΣI_+. The electrons return to the metal, the energy liberated being equal to the work function of the electron, ω_M^e. The work required to remove the ion into vacuum can thus be expressed as follows:

$$\omega_M^{Mz+} = S_M + \Sigma I_+ - z\omega_M^e \tag{9.65}$$

All the quantities entering into Eq. (9.65) are experimentally measurable, though not always with great accuracy. Thus, Gurney's formula offers, one would think, the fundamental possibility of calculating the absolute value of electrode potential from the energy characteristics of the metal and solution. It must however be kept in mind

that Gurney's theory, like the Nernst theory, defines not the whole electrode potential but only a part of it, i.e., the metal-solution potential difference. But even this quantity cannot be calculated on the basis of Gurney's theory since the latter does not take into account the potential difference which the ion crosses on its way from the vacuum into solution. The numerical value of this potential difference is known approximately, and therefore Gurney's formula determines the metal-solution potential difference with an accuracy up to a certain indefinite value.

Despite this drawback, the Gurney theory deserves attention. This theory made it possible to obtain the first realistic equation for the Volta potential at the metal-solution interface. The Volta potential between two metals is equal to the difference in the work functions of electrons for these metals [see Eq. (9.38)]. In deriving Eq. (9.38) no special assumptions were made restricting its sphere of relevance to a definite type of interface. For this reason it may be assumed that the Volta potential for an interface between any two phases is determined by the difference in the work required to remove the corresponding charged particles from both phases into vacuum. For a metal-solution interface such particles are ions.

Gurney's formula for the standard potential (9.64) is an equation which in fact defines the Volta potential across the solution-metal interface rather than the Galvani potential; it may be rewritten as

$$\psi_{LM} = \frac{Y^{M^{z+}} - A_r}{zF} = \frac{\omega_L^{M^{z+}} - \omega_M^{M^{z+}}}{zF} \tag{9.66}$$

where $A_r = -\Delta G_{h(r)}$ is the real energy of hydration. Since according to Eq. (3.22)

$$A_r = A_{ch} \pm zF\chi_{LV}$$

where A_{ch} is the chemical hydration energy and χ_{LV} the surface potential at the solution-vacuum interface, whose value is unknown, the absolute value of ψ_{LM} cannot be calculated from the Gurney formula. The latter can however be used as a basis for elucidating the effect of the nature of the solvent and the metal on the emf's of electrochemical cells and on conventional electrode potentials. These questions, which are of fundamental importance to electrochemistry, were thoroughly studied by Pleskov and Izmailov.

Izmailov makes use of Eq. (9.16)

$$E = \psi_{12} + \psi_{L2} - \psi_{L1}$$

which is valid for electrochemical cells of the type

$$M_1/M_1^{z+}//M_2^{z+}/M_2 \tag{9.67}$$

in which either there is no liquid junction or the diffusion potential has been eliminated. It is also applicable, for instance, to a cell

which determines the electrode potential of a metal on the arbitrary hydrogen scale:

$$\mathrm{Pt,\ H_2/H^+//M^{z+}/M} \tag{9.68}$$

Substituting into Eq. (9.16) the values of Volta potentials from Eqs. (9.38) and (9.66) and assuming that ${}_1z_+ = {}_2z_+ = z_+$ and $z_+ = = z_- = z$ and that the activities of the participants of the electrochemical reaction are equal to unity, Izmailov obtains:

$$E = \frac{\omega_1^e - \omega_2^e}{F} + \frac{\omega_1^{M_1^{z+}} + A_{r_1}}{zF} - \frac{\omega_2^{M_2^{z+}} + A_{r_2}}{zF} \tag{9.69}$$

or

$$E = \frac{\omega_1^e - \omega_2^e}{F} + \frac{\omega_1^{M_1^{z+}} + A_{ch_1}}{zF} - \frac{\omega_2^{M_2^{z+}} + A_{ch_2}}{zF} \tag{9.70}$$

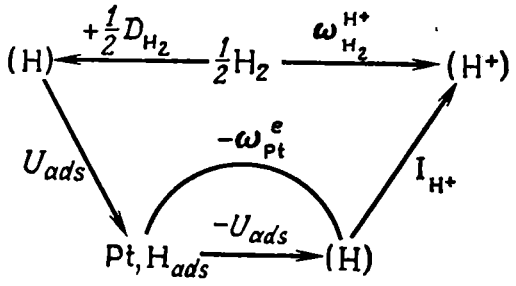
since from Eq. (3.22) it follows that

$$A_{r_1} - A_{r_2} = A_{ch_1} + zF\chi_{LV} - A_{ch_2} - zF\chi_{LV} = A_{ch_1} - A_{ch_2}$$

For the cell (9.67) the work functions of the metallic ions for the metal may be replaced by their values from the expression (9.65); then, after some rearrangement, one has:

$$E^0 = \frac{S_1 - S_2 + \Sigma I_{+(1)} - \Sigma I_{+(2)}}{zF} + \frac{A_{ch1} - A_{ch2}}{zF} \tag{9.71}$$

For the cell (9.68), which determines the standard potential of electrode M^{z+}/M on the arbitrary hydrogen scale, the value of $\omega_1^{M^{z+}}$, equal in this case to $\omega_{H_2}^{H^+}$, can be found from the following cycle



where D_{H_2} = energy of dissociation of hydrogen molecule
U_{ads} = energy of adsorption of hydrogen atoms on platinum
I_{H^+} = ionization potential of hydrogen atoms
ω_{Pt}^e = work function for electrons to be removed from platinum.

From the above cycle it follows that

$$\omega_{H_2}^{H^+} = \frac{1}{2} D_{H_2} + I_{H^+} - \omega_{Pt}^e \tag{9.72}$$

Substituting this value of $\omega_{H_2}^{H^+}$ for $\omega_1^{M_1^{z+}}$ into Eq. (9.70) and replacing A_{ch_1}, A_{ch_2} and $\omega_2^{M_2^{z+}}$ by $zA_{ch_{H^+}}$, $A_{ch_{M^{z+}}}$ and $\omega_M^{M^{z+}}$ and taking into

account Eq. (9.65), one obtains:

$$E^0_M = \frac{z\frac{1}{2}D_{H_2} - S_M + \Sigma z I_{H^+} - \Sigma I_{M^{z+}}}{zF} + \frac{zA_{ch_{H^+}} - A_{ch_{M^{z+}}}}{zF} \quad (9.73)$$

Equations (9.71) and (9.73) should be regarded as a mathematical expression of the basic propositions of the hydration (solvation) theory of electromotive forces and electrode potentials. The values of emf and standard electrode potential are represented as the sum of two terms. The first of them is governed by the properties of electrodes, and the second by the properties of potential-determining ions and the nature of the solvent.

Equations (9.71) and (9.73) can be employed to resolve many important problems pertaining to electrochemical equilibrium systems. For example, using Eq. (9.71), one can account for the dependence of the emf of the electrochemical cell (9.67) on the properties of the solvent. In this case the first term in Eqs. (9.71) and (9.73) remains constant, and the variation of the emf with the nature of the solvent is determined by the second term. Hence, Eqs. (9.71) and (9.73) may be rewritten in the form:

$$E^0 = \text{const} + \frac{A_{ch_1} - A_{ch_2}}{zF}$$

and

$$E^0 = \text{const} + \frac{zA_{ch_{H^+}} - A_{ch_{M^{z+}}}}{zF}$$

All theoretical equations for calculating the hydration energy contain the Born term

$$\frac{z^2e^2N_A}{2r}\left(1 - \frac{1}{D}\right)$$

and therefore the emf must be a function of the dielectric constant of the solvent, i.e., it must change from one solvent to another having a different dielectric constant. On the basis of the Born formula for the hydration energy one would expect a linear variation of E^0 with $1/D$. This was first suggested by Brodsky, who deduced a corresponding equation for emf. The experimental investigations carried out by Brodsky, Izgaryshev, Pleskov, and Izmailov have shown that this assumption can only serve as a first approximation. This result should be considered legitimate since the Born term does not cover the whole hydration energy, which includes also specific interaction forces. A theoretical calculation of the hydration energies of individual ions is a complicated problem that has not yet been solved. It would be more reasonable to use Eq. (9.70) for solving the reverse problem, i.e., estimating the changes of the chemical energy of hydration from solvent to solvent by using experimentally determined values of electromotive force.

PART FOUR

The Electrical Double Layer at the Electrode-Electrolyte Interface

In the preceding sections we discussed the following; (a) the physical meaning of the electrode potential; (b) its relation with potential differences at phase boundaries; (c) the conditions under which a potential difference develops across an electrode-electrolyte interface (this p.d. being the principal part of the electrode potential); and (d) the dependence of the value of this p.d. on the composition of the solution. In considering the mechanism by which a potential difference develops at the electrode-electrolyte interface it was stated that the main factor responsible for its appearance is the exchange of ions between an electrode metal and the solution. This process at first (i.e., at the moment the metal and solution are brought into contact) involves nonequivalent amounts of ions, as a result of which the two contiguous phases acquire excess-charge densities of opposite sign and an electrical double layer is formed. But we have not yet examined the structure of the electrical double layer and the charge distribution on the two sides of the interface. The structure of the double layer is of no decisive importance to the value of equilibrium electrode potential, which is determined by the free-energy change in the corresponding electrochemical reaction. At the same time the structure of the double layer plays an important role in the kinetics of electrode processes, including that of ion exchange in equilibrium conditions because its intensity (the exchange current I^0) depends on the structure of the double layer. The theory of the structure of the double layer therefore serves as a sort of an intermediate link between electrode equilibrium and electrode kinetics.

An important contribution to the formation of the present-day conceptions of the double-layer structure has been made by investigators of electrokinetic and electrocapillary phenomena.

CHAPTER 10

Electrokinetic and Electrocapillary Phenomena

10.1. ELECTROKINETIC PHENOMENA

Electrokinetic phenomena reflect the relation between the relative motion of two phases (most often, a liquid and a solid) and the electrical properties of the interface between them. Electrokinetic phenomena arise in those cases when one phase is dispersed in the other, i.e., when the system can be described as microheterogeneous. Four groups of electrokinetic phenomena are distinguished: *electroosmosis*, *electrophoresis*, *streaming potential*, and *sedimentation potential* (Table 10.1).

TABLE 10.1

Classification of Electrokinetic Phenomena

Phenomenon	Description	Cause
Electroosmosis	Movement of a liquid along a solid (a capillary, system of capillaries or porous plug)	An externally applied electric field
Electrophoresis	Movement of solid particles dispersed in a liquid	An externally applied electric field
Streaming potential	Formation of a potential difference between the upstream and downstream ends of liquid flow	Movement of a liquid along a solid (a capillary, system of capillaries or porous plug)
Sedimentation potential (precipitation potential)	Formation of a potential difference between the top and the bottom of a vessel in which dispersed solid particles are suspended in a liquid	Sedimentation of solid particles suspended in a liquid (movement of solid particles relative to a stationary liquid phase)

The discovery of electrokinetic phenomena is due to F. Reuss, whose experiments on electroosmosis and electrophoresis were described in 1809 in the Proceedings of the Moscow Society of Naturalists.

The other two effects (streaming potential, which is the converse of electroosmosis, and sedimentation potential, the converse of ele-

ctrophoresis) were discovered by Quincke (1859) and Dorn (1878) [1].

The electrokinetic effects, especially electroosmosis and electrophoresis [2], find use in many processes, for example, in dehydration and purification of various materials; deposition of rubber, leather and other coatings onto nonconducting materials; impregnation of textiles with fire-resistant compounds; determination and separation of enzymes, proteins, viruses, and other complex systems.

The occurrence of electrokinetic phenomena is an indication that there is an electrical double layer at the boundary between a solid and a liquid, both these phases being electrically charged. The movement of suspended solid particles inside the liquid under the influence of an applied electric field (electrophoresis) is only possible when the solid particles distributed in the liquid are electrically charged. Similarly, the electroosmotic movement of the liquid would be impossible if it had no charge, which is affected by an electric field. No potential difference would arise between points at different heights in a tube where sedimentation of the solid particles suspended in the liquid occurs if the precipitating particles had no electrical charge. And, finally, one cannot account for the appearance of a streaming potential without assuming that the liquid possesses a certain charge.

A study of the relation existing between the direction and velocity of electrophoresis or electroosmosis, on the one hand, and the direction and strength of the applied electric field, on the other, can yield information on the sign and magnitude of the charge of the solid particles with respect to the liquid and on the corresponding potential difference.

The approximate theory of electrokinetic phenomena provides the following equations for the electroosmotic velocity U and the streaming (or sedimentation) potential E:

$$U = \frac{D}{4\pi\gamma} \frac{\Delta\psi}{\Delta x} \zeta \tag{10.1}$$

and

$$E = \frac{DP}{4\pi\gamma\varkappa_0} \zeta \tag{10.2}$$

$$E = \frac{DP}{4\pi\gamma} \Omega \frac{\Delta\psi}{\Delta x} \zeta \tag{10.2a}$$

where D = dielectric constant of the liquid phase
$\Delta\psi/\Delta x$ = electric field strength in the direction parallel to the interface between the liquid and solid phases
γ = viscosity of the liquid phase
$\varkappa_0$ = conductivity of the liquid phase

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[1] The phenomenon of sedimentation potential is also known as the *Dorn effect*.—*Tr.*

[2] These two phenomena are also called ***electroendosmosis*** and ***cataphoresis***, respectively.—*Tr.*

P = pressure causing the relative movement of the phases along the interface

Ω = cross-section of the suspended particle (or pore).

In the case of electrophoresis

$$P = gM\left(1 - \frac{d_L}{d_S}\right) \tag{10.3}$$

where g = acceleration due to gravity

M = mass of the suspended particles passing through a unit cross-sectional area (1 cm^2) of the microheterogeneous system

d_L and d_S = densities of the liquid and suspended solid particles, respectively.

The quantity ζ in Eqs. (10.1) and (10.2) is called the *electrokinetic* or *zeta potential*; it can be found with the aid of Eqs. (10.1) and (10.2) if the quantity U or E is known. It is however necessary to remember that these equations are approximate, and hence the value of ζ can be estimated only roughly. Direct measurements yield $D\zeta/\gamma$ rather than ζ, and the calculated value of ζ depends on the numerical values of D and γ. The values of the dielectric constant and viscosity of the liquid phase which are substituted into Eqs. (10.1) and (10.2) may be different from those observed in the immediate vicinity of the interface. The ζ potentials calculated from these equations may therefore differ markedly from their true values. Besides, the field strength and conductivity of the liquid near the interface [i.e., the quantities that would be used in calculating the zeta potential from Eqs. (10.1) and (10.2)] and in the bulk of the liquid phase do not coincide in a general case. This difference is due to the fact that the ionic composition at the phase boundary is usually different from the average ionic composition of the whole liquid phase. This is reflected in the appearance of so-called surface conductance $\varkappa'$. Bikerman pointed out that the appearance of surface conductance is responsible for the fact that the field strength near the interface, $(\Delta\psi/\Delta x)_{LS}$, is usually lower than the average macroscopic field strength, the quantity $(\Delta\psi/\Delta x)_{LS}$ being given by

$$\left(\frac{\Delta\psi}{\Delta x}\right)_{LS} = \frac{\frac{\Delta\psi}{\Delta x}}{1 + \frac{\varkappa' l}{\varkappa_0 \Omega}} \tag{10.4}$$

where l is the perimeter of the pore or particle.

It was formerly thought that the zeta potential of colloid chemistry is equivalent to the electrode potential (or the ε potential) of electrochemistry, more exactly, to that part of the electrode potential which represents the potential difference at the electrode-electrolyte interface. This thinking was based on the nature of electrokinetic

phenomena. Indeed, if the liquid-solid interface is also a *surface of shear* (or *slipping plane*) during the movement of the phases relative to each other, the zeta potential must be equal to the ε potential or, more precisely, to the potential difference g_{LM}. If this assumption were valid and in agreement with experiment, it would be possible to measure the electrode-electrolyte potential difference experimentally and to determine the absolute electrode potential. It is however impossible to check the validity of this assumption by direct comparison of the independently found values of the ζ and g_{LM} potentials since the Galvani potential g_{LM} is experimentally inaccessible. But it is possible to check it indirectly by comparing the dependences of the ζ and ε potentials on the solution composition.

Since g_{LM} is the only constituent part of the electrode potential that depends on the electrolyte concentration, it follows that with the equality $\zeta = g_{LM}$ being satisfied the variation of the ζ and ε potentials with concentration must be the same and obey the same law. Such a comparison can be made, for example, as follows. First, an insoluble solid is ground and the electrophoretic velocity of the resulting particles in a solution of variable electrolyte concentration is measured. This being done, the zeta potential is determined as a function of the concentration. Then the same solid is used as an electrode in the same solutions and its ε potential is measured on the hydrogen scale. Such experiments have been carried out by many investigators and all the results obtained show that the zeta potential cannot be identified with the electrode potential. For example, Freundlich (1925) conducted experiments with glass, using it first as an electrode for determining the ε potential and then as thin capillaries for causing electroosmosis and calculating the zeta potential. The dependences of the ε and ζ potentials on the concentration of potassium chloride and thorium nitrate obtained by Freundlich are presented in Fig. 10.1. It can be seen from the figure that ε and ζ vary with concentration according to different laws. The zeta potential is found to vary with concentration not monotonically but, in contrast to ε, passes through a minimum or maximum. The zeta potential is usually smaller in absolute value than ε and tends to zero with increasing concentration. Whereas the sign of ε remains unchanged over a wide range of concentrations, the sign of ζ may be reversed, and the sooner, the higher the valency of the ions and the stronger their ability for selective adsorption. As a result of the reversal of the sign of ζ (so-called "recharging" of the surface) it may be either similar or opposite to the sign of the electrode potential for the same interface. Hence, the zeta potential differs in its nature from the electrode potential. On the basis of the properties of the zeta potential one can conclude that it is a fraction of that part of the total potential difference which is completely within the liquid phase. It is because the zeta potential, unlike ε, lies in one and the same

phase that the experimental determination of its absolute value is possible. The potential drop corresponding to ζ must be confined to the interface between the liquid layer immediately adjacent to the

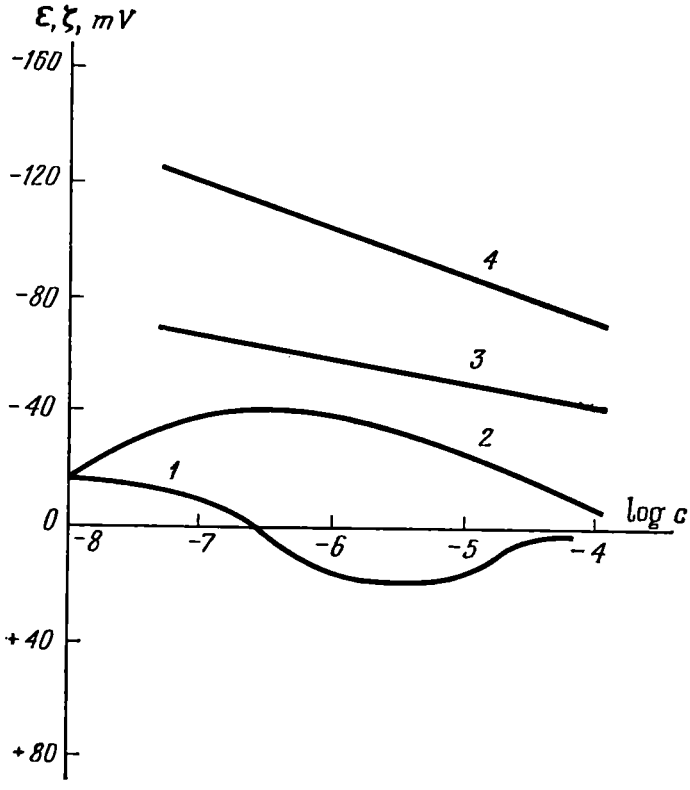

Fig. 10.1. Variation of ζ potential (curves *1* and *2*) and ε potential (curves *3* and *4*) with concentration of thorium nitrate (*1* and *4*) and potassium chloride (*2* and *3*)

solid surface (and bound with it during the relative motion of the liquid and solid phases) and deeper liquid layers away from the interface.

In this connection, at given compositions of the solution and solid phase the value of ζ must be a function of the topography of the interface. The surface of a solid is never ideally smooth, there are always hills and valleys. The height of hills varies within wide limits depending on the nature of the solid surface. This height usually ranges from 100 Å for exceptionally well-polished, to 20,000 Å for visibly rough surfaces. In valleys, there appear stagnant zones where the laminar flow of the liquid is obstructed and part of its charges (which is the larger, the deeper the valley) is immobilized, and the zeta potential is depressed accordingly.

The fact that, in addition to the total potential difference, there also exists a zeta potential between a solid and a solution should be

taken into account in working out the theory of the electrical double layer. This theory must explain not only the occurrence of the electrokinetic potential but also the mode of its variation with the solution composition and, in particular, the recharging of the surface.

10.2. ELECTROCAPILLARY PHENOMENA

10.2.1. GENERAL DESCRIPTION

When two phases are brought into contact, a boundary layer (or interphase region) is formed. It has an excess of free energy compared with each of the two contiguous phases. The excess energy referred to a unit surface area of the interface, i.e., the specific free energy, is called the *surface tension* σ (or the *interfacial tension* [1]); it has the dimensions of $erg \cdot cm^{-2}$ or $dyne \cdot cm^{-1}$. The surface tension is often treated as a quantity characterizing the excess of the forces of mutual attraction over the repulsive forces. The excess surface energy depends on the potential difference between two phases. Electrocapillary phenomena reflect the relation between the surface tension and the interfacial potential difference. This relation is graphically expressed in the form of electrocapillary curves. Electrocapillary effects were first studied at the interface between mercury and aqueous electrolytic solutions by Lippmann (1875), who used a capillary electrometer of his own design for this purpose. His studies were continued by Gouy (1910) and Frumkin (1919) and also by a number of other investigators (including Butler, Kruger, Grahame, Parsons).

In electrocapillary measurements using a capillary electrometer, a definite potential is applied to a mercury microelectrode in the capillary (in contact with the solution) and the height of the mercury column required to keep the meniscus in the capillary at the reference mark is measured. The potential across the mercury-solution interface in the capillary is provided by imposing a specified emf (for example, through a potentiometer) on an electrochemical system in which one electrode is a capillary electrode and the other, the corresponding reference electrode of known potential. Since the reference electrode is nonpolarizable, its potential remains unchanged, while the ideally polarizable capillary mercury electrode acquires a potential corresponding to the externally applied emf [2]. As follows

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[1] The two terms *surface tension* and *interfacial tension* are used interchangeably here, though, strictly speaking, it is interphasial (determined by both phases) rather than surface tension.—*Tr.*

[2] A nonpolarizable electrode is an electrode for which the exchange of potential-determining ions between the metal and solution proceeds unhindered (this is observed at high exchange-current densities). The potential of such an electrode remains practically unchanged under the effect of an external current as long as the applied current is small compared with the exchange current. The

from the theory of capillarity, the height of the mercury column above the mercury meniscus in the capillary is a measure of surface tension at the mercury-solution interface. The relation between these two quantities may be written in the following form

$$2\pi r\sigma = \pi h r^2 g d \tag{10.5}$$

whence

$$\sigma = \frac{h}{2} rgd \tag{10.6}$$

where r = capillary radius
g = acceleration due to gravity
d = density of mercury.

By measuring the height h at different values of the potential and calculating the corresponding values of σ from Eq. (10.6) one can plot an electrocapillary curve. The shape of electrocapillary curves for a number of dilute solutions (e.g. H_2SO_4, KOH, KNO_3, Na_2SO_4) is almost independent of the nature of the electrolyte and is almost a parabola. The maximum on the curve is observed at approximately the same value of potential within the range from —0.19 to —0.21 V on the hydrogen scale. The interfacial tension at the maximum also changes little in going from one of the indicated solutions to another and amounts to 420-430 ergs·cm^{-2}. For example, according to Gouy, at 18° C in a 0.01 N Na_2SO_4 solution and in pure water σ = = 426.7 dynes·cm^{-1}. Electrocapillary curves traced for solutions of other electrolytes and also in the presence of most of the organic unionized substances are radically different in shape from a parabola. They are less symmetrical and their maxima are situated at other values of ε and σ.

Along with electrocapillary curves for electrolytes of the KNO_3 type, Fig. 10.2 shows curves for those cases when Br^-, I^-, S^{2-}, Tl^+ or $N(C_3H_7)_4^+$ ions, or molecules of amyl alcohol are present in the solution. The presence of bromide, iodide or sulphur ions shifts the electrocapillary maximum (ecm) towards more negative values of

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(hypothetical) ideally polarizable electrode is one for which the ion exchange is completely or almost completely inhibited and the exchange current density is close to zero. For such an electrode, even a negligibly small external current will affect the potential. Under the conditions of electrocapillary measurements the mercury electrode behaves like the ideally polarizable electrode, though the exchange current density between the metallic mercury and a solution of its salt is very great at equilibrium. This is attributable to two causes: first, the region of potentials for which electrocapillary curves are plotted is displaced to the negative side from the equilibrium potential of the mercury electrode, and therefore the anodic process of transfer of mercury ions from the metal into solution is thermodynamically improbable; second, electrocapillary curves are traced for solutions practically devoid of mercury ions. Under these conditions the cathodic process of transfer of mercury ions from the solution to the metal is also impossible.

potential and (especially in the region of potentials situated on the left of the maximum) lowers the surface tension. At sufficiently negative potentials the effect of these anions disappears and the electrocapillary curves merge together. The presence of thallium or tetrabutylammonium ions displaces the electrocapillary maximum to the side of more positive values and reduces the surface tension, this reduction being especially pronounced at potentials more negative than the potential of the electrocapillary maximum. The effect of these cations disappears as soon as sufficiently positive potentials

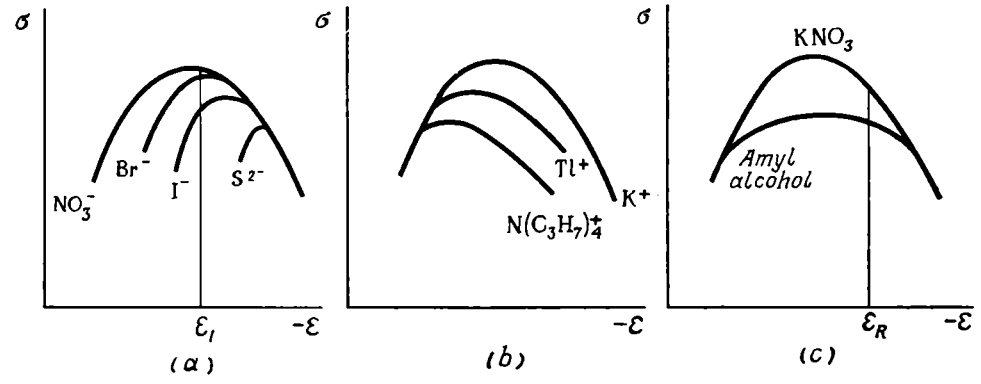

Fig. 10.2. Electrocapillary curves for solutions containing surface-active anions (*a*), cations (*b*), and molecular substances (*c*)

are attained. The presence of amyl alcohol causes a change in the shape of the electrocapillary curve mainly in the region of potentials adjacent to the ecm potential. With increasing distance on either side of the potential of the electrocapillary maximum the effect of addition of amyl alcohol diminishes and the curve traced in the presence of amyl alcohol coincides with the curve for a pure solution. Ionic or molecular compounds exerting such an effect are called *specifically adsorbed* or *capillary-active ions* or *molecules* [1].

The electrocapillary properties of the mercury-solution interface may be explained by assuming that at a potential ε_1 and in the absence of an external emf mercury is positively charged with respect to the solution (Fig. 10.3*a*). The excess positive charge of mercury is most probably associated with the mercury ions residing at its surface (on the metal side). The system as a whole as well as its interphase must obey the law of electroneutrality. There will therefore be an excess of negative ions on the solution side at the interface, which will compensate for the positive mercury ions on the metal. The presence of like-charged (positive) mercury ions on the metal surface

[1] Recent data indicate that at the] mercury-solution interface all anions, except the fluoride ion F^-, are capillary-active. The capillary activity of NO_3^- and SO_4^{2-} and some other anions however is very low and may be ignored in most cases.

inevitably gives rise to repulsive forces, and the surface tension at the mercury-solution interface cannot be high; in Fig. 10.3 it is denoted by σ_1.

When an external emf is applied, the potential of the mercury is shifted (as a result of its cathodic polarization) to the side of more negative values, say, to the value ε_2 (Fig. 10.3*b*). Part of the mercury ions is neutralized by electrons and the charge on the mercury diminishes accordingly, but it still remains positive. The repulsive forces between the surface mercury ions will become smaller and hence

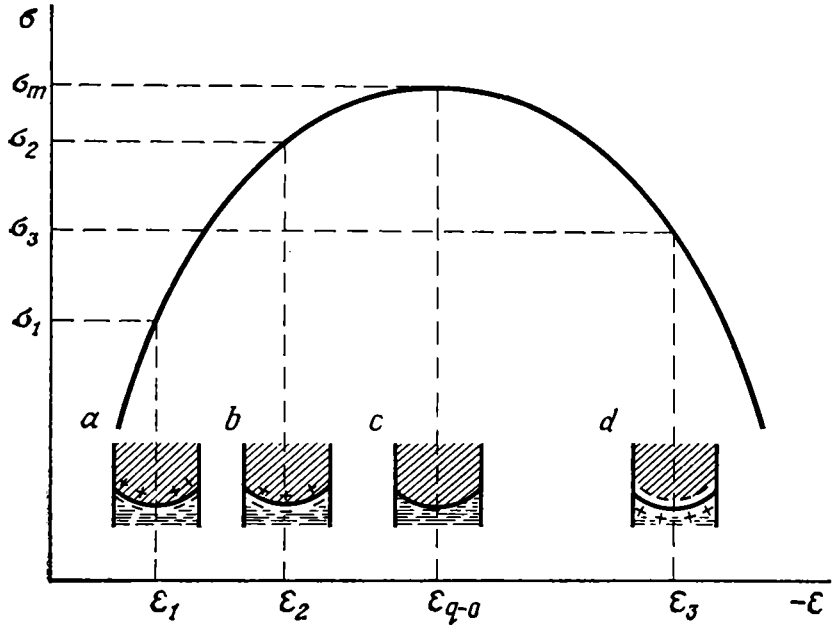

Fig. 10.3. Variation of the surface charge of mercury during transition from the ascending to the descending branch of the electrocapillary curve

the interfacial tension will increase, say, to the value σ_2. The number of negative ions attracted to the mercury surface from the solution side will simultaneously be reduced. At a definite value of the potential $\varepsilon = \varepsilon_{q=0}$ the positive charges of all the mercury ions will be compensated for by electrons and the charge on the mercury surface will become equal to zero; at the same time (if there are no capillary-active particles in the solution) the charge of the solution will also become zero (Fig. 10.3*c*). The repulsive forces associated with the presence of like-charged particles on the mercury surface will disappear as soon as these particles are neutralized, and the interfacial tension will assume a certain value σ_m. Upon further shift of the mercury potential to the negative side (to the value ε_3) an excess of electrons will appear on the mercury surface; they will attract positively charged ions from the solution side. Repulsive forces

will again appear between like-charged (this time, negative) particles, and the interfacial tension will fall down to a certain value (σ_3). With increasing negative value of potential the excess negative charge of the mercury increases and the interfacial tension diminishes. The ascending branch of the electrocapillary curve thus pertains to the positively charged mercury surface. The magnitude of the positive charge gradually decreases as the potential shifts to the negative side, while the interfacial tension increases accordingly. At the maximum of the electrocapillary curve the charge on the mercury surface is zero, whereas the interfacial tension attains the highest value. The descending branch of the curve corresponds to the negatively charged mercury surface. With increasing distance from the ecm the absolute magnitude of the charge increases and the interfacial tension is lowered. Thus, the concept of the variation of the charge on the mercury with the potential of the mercury electrode permits a qualitative explanation of the course of the electrocapillary curve for solutions containing no capillary-active particles.

If one starts from the assumption that the adsorption of ions on mercury depends exclusively on electrostatic forces, all the anions should be expected to affect only the ascending (positive) branch where the mercury surface is charged positively. Conversely, the effect of cations should be confined to the descending (negative) branch, where they are electrostatically attracted to the negatively charged mercury surface. In fact, as was observed by Gouy, many anions change the path of the electrocapillary curve on the right of the maximum and some cations affect not only the descending but also the ascending branch. This behaviour of ions cannot be ascribed to the action of coulombic forces alone. It is associated with interaction forces other than simple electrostatic forces. Such forces, which are specific to particles of a given species, may be, for example, van der Waals forces or chemical (valence) forces. Because of these forces ions are capable of sticking on the like-charged mercury surface and affecting the electrocapillary properties of the metal-solution interface. Similarly the influence of unionized organic substances on the course of electrocapillary curves cannot be explained on the basis of electrostatic concepts alone. The point is that most organic substances possess a lower dielectric constant than water and should therefore be expelled by it from the double layer even at small charges, just as a dielectric material with a lower dielectric constant is expelled from a charged capacitor by a dielectric with a higher constant. In this case the effect of organic substances would be expected to manifest itself only within a narrow region of potentials adjacent to the electrocapillary maximum. Actually, a change in the shape of the electrocapillary curve due to organic substances is observed even at potentials distant 0.5-0.8 V from the ecm potential on either side, i.e., some specific forces must be operating here. The

term "specifically adsorbed particles" introduced earlier thus implies that the behaviour of such particles at the mercury-solution interface cannot be attributed only to forces of electrostatic origin.

10.2.2. THE FOUNDATIONS OF THE THEORY OF ELECTROCAPILLARY PHENOMENA

An equation which describes well the shape of electrocapillary curves and establishes the relation between interfacial tension, potential and charge at the mercury-solution interface was derived by Lippmann:

$$-\frac{d\sigma}{d\varepsilon} = q_{Hg} \qquad (10.7)$$

This equation, known as *Lippmann's first equation*, defines the slope at each point of the electrocapillary curve, taken with opposite sign, as a quantity equal to the specific charge q_{Hg} on the mercury surface at a given value of potential ε [1]. In accord with the qualitative picture of electrocapillary phenomena, it follows from Eq. (10.7) that on the ascending branch of the curve $q_{Hg} > 0$ ($d\varepsilon$ is always smaller than 0; on the ascending branch $d\sigma > 0$, whence $d\sigma/d\varepsilon < 0$ or $-d\sigma/d\varepsilon > 0$), at the maximum $q_{Hg} = 0$ (since $d\sigma/d\varepsilon = 0$), and on the descending branch $q_{Hg} < 0$ ($-d\sigma/d\varepsilon < 0$). Using Lippmann's first equation, one can calculate the charge at any value of potential from experimental electrocapillary curves and construct graphs of the charge on the mercury surface versus potential. Since the charge is directly measurable, it is possible to check the validity of the Lippmann equation. To do this, one has to compare calculated and observed values of the charge. This checking was done by Frumkin. The results obtained by him show that the Lippmann equation is quantitatively applicable to electrocapillary curves.

Since Eq. (10.7) yields the magnitude of the charge irrespective of its origin, it can be applied to electrocapillary curves obtained for any solutions, including those containing capillary-active substances. At one and the same potential, say, at ε_1 (in Fig. 10.2*a* it is represented by a vertical line), both the magnitude and the sign of the charge may be different, depending on the nature of the particles in solution. It is negative in a KNO_3 solution, equal to zero in a solution of KBr, and positive in KI and K_2S solutions. Thus, analysis of electrocapillary curves as well as the data obtained from studies of electrokinetic phenomena points to the possibility of recharging

[1] According to the law of electroneutrality the charge on the metal surface must be equal in magnitude but opposite in sign to the charge of the solution at the interface, i. e., $q_M = -q_L$. Hence, Eq. (10.7) permits also determination of the magnitude of the charge for that part of the double layer which is in the solution.

of a metal surface in the presence of capillary-active substances with the total potential difference across the metal-solution interface remaining unaltered.

It is known that the derivative of the charge with respect to the potential is the differential capacity C_d, i.e., a quantity characterizing the variation of charge with potential:

$$\frac{dq}{d\varepsilon} = C_d \tag{10.8}$$

The value of the differential capacity can also be found with the aid of electrocapillary curves. Indeed, from Eqs. (10.7) and (10.8) it follows that

$$-\frac{d^2\sigma}{d\varepsilon^2} = \frac{dq}{d\varepsilon} = C_d \tag{10.9}$$

This expression is known as *Lippmann's second equation.*

Equation (10.8) may be represented in the form:

$$dq = C_d\, d\varepsilon \tag{10.10}$$

Since at the electrocapillary maximum $q = 0$ and $\varepsilon = \varepsilon_{ecm}$, it follows that after integration of Eq. (10.10)

$$\int_0^q dq = \int_{\varepsilon_{ecm}}^{\varepsilon} C_d\, d\varepsilon \tag{10.11}$$

one obtains

$$q = C\,(\varepsilon - \varepsilon_{ecm}) \tag{10.12}$$

or

$$C = \frac{q}{\varepsilon - \varepsilon_{ecm}} \tag{10.13}$$

where C is the integral capacity at the potential ε. Figure 10.4 shows an electrocapillary curve and the corresponding metal charge-potential and differential capacity-potential curves calculated from Eqs. (10.7) and (10.9). The curves in Fig. 10.4 are typical of solutions of capillary-inactive electrolytes. In this case, in the range of potentials corresponding to the ascending branch of the curve, the capacity changes comparatively little after the first abrupt fall and varies from 20 to 40 μF/cm². On approaching the electrocapillary maximum the capacity decreases, passes through a minimum (which is the more pronounced, the lower the concentration of the electrolyte) and then, after a certain rise, remains almost constant (about 20 μF/cm²) over a wide range of potentials on the descending branch of the curve. The addition of capillary-active substances affects not only the electrocapillary curve but also the curves showing the variation of charge and capacity with potential. For instance, in the presence

of organic substances the differential capacity-potential curve has an indistinct minimum lying at lower values of capacity than in the case of solutions of capillary-inactive electrolytes. A sharply defined maximum is observed on capacity-potential curves at a potential at

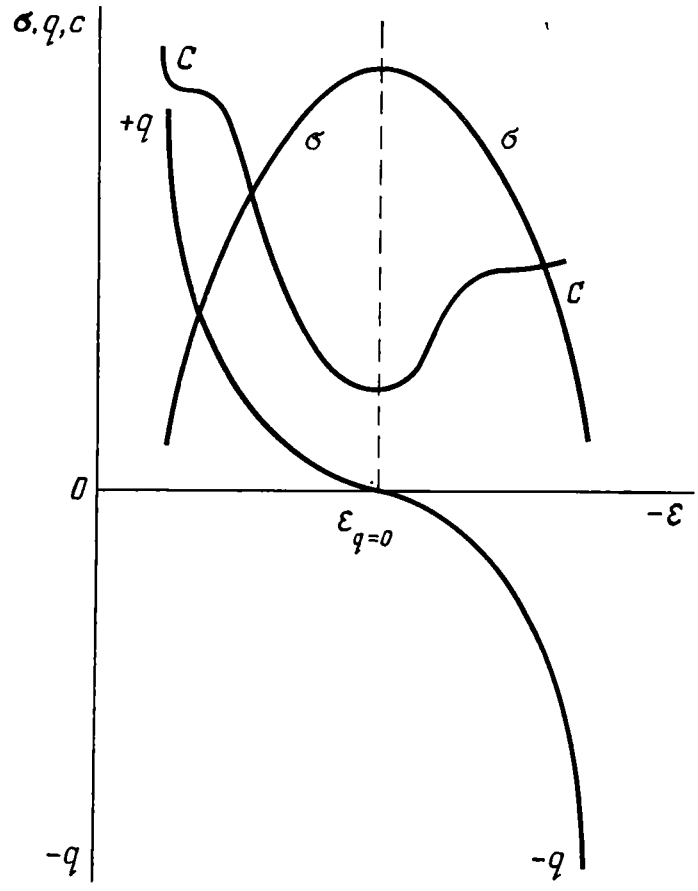

Fig. 10.4. Typical curves:
interfacial tension (σ) vs. potential (ε); surface charge (q) vs. potential (ε); and double-layer capacity (C) vs. potential (ε) for the interface between mercury and a solution of a capillary-inactive electrolyte

which the electrocapillary curves obtained with and without an organic substance merge into a single curve (the desorption potential).

The interfacial tension is a function of the solution composition. This functional dependence was expressed mathematically by Gibbs on the basis of the termodynamics of the surface layer formed at the phase boundary and, as mentioned before, is often called the interphase region or simply interphase. The Gibbs free energy for an interphase is given by

$$dG = V\,dP - S\,dT - \Sigma N_i\,d\mu_i$$

where V = volume
S = entropy of the interphase
N_i = number of particles of a species i in the interphase.

If the surface area of the interface is Ω_{int}, then the free energy referred to a unit surface area will be equal to

$$\frac{dG}{\Omega_{int}} = \frac{V}{\Omega_{int}} dP - \frac{S}{\Omega_{int}} dT - \frac{1}{\Omega_{int}} \Sigma N_i \, d\mu_i$$

or

$$d\sigma = l_{int} \, dP - S_{int} \, dT - \Sigma \Gamma_i \, d\mu_i \qquad (10.14)$$

where l_{int} = thickness of the interphase
S_{int} = entropy referred to a unit surface area of the interface
Γ_i = surface concentration of the ith component.

If the interphase is in a volume-mechanical and thermal equilibrium, then $dP = 0$ and $dT = 0$, and Eq. (10.14) simplifies to

$$d\sigma = -\Sigma \Gamma_i \, d\mu_i \qquad (10.15)$$

which corresponds to the Gibbs adsorption formula.

Summation in Eq. (10.15) must be carried out over all the components (both ionic and molecular) forming the interphase region on both sides of the phase boundary [1]. Since a number of limitations are imposed on the system (the law of electroneutrality, equilibrium between dissociated and initial molecules, etc.), the actual number of variables will be less than the total number of components. The conditions for the application of Eq. (10.15) to electrocapillary phenomena were worked out in detail by Grahame (1942) and Parsons (1953).

The Lippmann equation can be derived from the Gibbs adsorption formula and the Nernst formula for electrode potential by making certain assumptions. If the charge on mercury is assumed to be determined by the surface concentration of mercury ions Γ_{Hg^+} [2] and the term corresponding to these ions is extracted from the sum on the right-hand side of Eq. (10.15), then

$$d\sigma = -\Gamma_{Hg^+} \, d\mu_{Hg^+} - \Sigma \Gamma_i \, d\mu_i \qquad (10.16)$$

Taking into account that

$$\Gamma_{Hg^+} F = q$$

Eq. (10.16) may be rewritten in the form

$$d\sigma = -\frac{q}{F} d\mu_{Hg^+} - \Sigma \Gamma_i \, d\mu_i \qquad (10.17)$$

---

[1] For charged particles the electrochemical potential μ_{ech} should be used instead of the chemical potential μ.

[2] The surface charge is determined by the difference in the surface concentrations of mercury ions and electrons, i.e., by the quantity $(\Gamma_{Hg^+} - \Gamma_e) F$, and therefore Γ_{Hg^+} is here the *surface excess* of mercury ions.

Since

$$\mu_{Hg^+} = \mu^0_{Hg^+} + RT \ln a_{Hg^+}$$

and the potential of the mercury electrode

$$\varepsilon_{Hg^+/Hg} = \varepsilon^0_{Hg^+/Hg} + \frac{RT}{F} \ln a_{Hg^+}$$

the following relation must be satisfied:

$$d\mu_{Hg^+} = F\, d\varepsilon_{Hg^+/Hg} \tag{10.18}$$

Substituting the value of $d\mu_{Hg^+}$ from Eq. (10.18) into Eq. (10.17) gives

$$d\sigma = -q\, d\varepsilon - \Sigma \Gamma_i\, d\mu_i \tag{10.19}$$

If the composition of the solution remains constant, then by the Gibbs-Duhem equation (I.45)

$$\Sigma \Gamma_i\, d\mu_i = 0$$

and Eq. (10.19) simplifies to

$$d\sigma = -q\, d\varepsilon \tag{10.20}$$

which coincides with Lippmann's first equation.

The use of Eq. (10.15) can be demonstrated on the following cell

$$M'/Ag,\ AgCl/KCl,\ H_2O/Hg/M \tag{10.21}$$

The quantity $d\sigma$ in Eq. (10.15) will be determined by all the components (both charged and neutral) responsible for the attainment of an equilibrium between mercury and solution, i.e.,

$$-d\sigma = \Gamma_{Hg^+}\, d\mu^{Hg^+}_{ech\,(Hg)} + \Gamma_e d\mu^{e}_{ech\,(Hg)} + \Gamma_{K^+} d\mu^{K^+}_{ech\,(L)} + \\ + \Gamma_{Cl^-} d\mu_{ech(L)} + \Gamma_{H_2O}\, d\mu^{H_2O}_{L} \tag{10.22}$$

The charge on the mercury surface with respect to the solution is given by the equation

$$q = F\,(\Gamma_{Hg^+} - \Gamma_e) \tag{10.23}$$

It is equal in magnitude and opposite in sign to the charge of the solution with respect to mercury

$$-q = F\,(\Gamma_{K^+} - \Gamma_{Cl^-}) \tag{10.24}$$

The equilibrium inside the mercury is given by the equation

$$\mu^{Hg}_{Hg} = \mu^{Hg^+}_{ech\,(Hg)} + \mu^{e}_{ech\,(Hg)} \tag{10.25}$$

and that between the mercury and conductor M, by the equation

$$\mu^{e}_{ech\,(Hg)} = \mu^{e}_{ech\,(M)} \tag{10.26}$$

Inside the solution there exists an equilibrium between KCl and the K^+ and Cl^- ions:

$$KCl = K^+ + Cl^-$$

and

$$\mu_L^{KCl} = \mu_{ech\,(L)}^{K+} + \mu_{ech\,(L)}^{Cl-} \tag{10.27}$$

Besides, the Cl^- ions are in equilibrium with AgCl

$$Ag + Cl^- = AgCl + e_{Ag}^-$$

and

$$\mu_{Ag}^{Ag} + \mu_{ech\,(L)}^{Cl-} = \mu_{AgCl}^{AgCl} + \mu_{ech\,(Ag)}^{e}$$

or

$$d\mu_L^{Cl-} = d\mu_{Ag}^{e} = d\mu_{M'}^{e} \tag{10.28}$$

since $d\mu_{Ag}^{Ag} = 0$ and $d\mu_{AgCl}^{AgCl} = 0$ and the silver is in contact with metal M′.

Combining Eq. (10.22) with Eqs. (10.23) through (10.28), one gets

$$-d\sigma = \frac{q}{F} d\mu_{ech(M')}^{e} - \frac{q}{F} d\mu_{ech(M)}^{e} + \Gamma_{Hg^+} d\mu_{Hg}^{Hg} + \\ + \Gamma_{K^+} d\mu_L^{KCl} + \Gamma_{H_2O} d\mu_L^{H_2O} \tag{10.29}$$

Since the right-hand electrode is pure mercury, μ_{Hg}^{Hg} must be a constant quantity, i.e., $d\mu_{Hg}^{Hg} = 0$, and hence

$$\Gamma_{Hg^+} d\mu_{Hg}^{Hg} = 0 \tag{10.30}$$

Further, the difference between the differentials of the electrochemical potentials of the electrons in two phases M and M′ having the same chemical composition can be represented, using Eq. (9.20), in the following form

$$d\mu_{ech\,(M)}^{e} - d\mu_{ech\,(M')}^{e} = Fd\,(g_{M'}^{e} - g_{M}^{e}) = F\,d\varepsilon_- \tag{10.31}$$

where the minus subscript for ε signifies that the reference electrode is reversible with respect to the electrolyte anions (in our case to chloride ions).

Taking account of Eqs. (10.30) and (10.31), one can write, in place of Eq. (10.29),

$$-d\sigma = q\,d\varepsilon_- + \Gamma_{K^+} d\mu_L^{KCl} + \Gamma_{H_2O} d\mu_L^{H_2O} \tag{10.32}$$

According to the Gibbs-Duhem equation

$$x_{KCl}\,d\mu_{KCl} + x_{H_2O}\,d\mu_{H_2O} = 0$$

where x is the corresponding mole fraction. Consequently,

$$-d\sigma = q\,d\varepsilon_- + \left(\Gamma_{K^+} - \frac{x_{KCl}}{x_{H_2O}} \Gamma_{H_2O}\right) d\mu_L^{KCl} \tag{10.33}$$

The expression in parentheses yields the surface excess of potassium ions relative to water; denoting it by $\Gamma_{K^+(H_2O)}$, or simply [1] by Γ_{K^+}, we have

$$-d\sigma = q\,d\varepsilon_- + \Gamma_{K^+}\,d\mu_L^{KCl} \qquad (10.34)$$

If in the cell (10.21) the silver-silver chloride electrode is replaced with an amalgam electrode reversible with respect to potassium ions, one can, by reasoning as before, obtain the following equation, in place of Eq. (10.34),

$$-d\sigma = q\,d\varepsilon_+ + \Gamma_{Cl^-}d\mu_L^{KCl} \qquad (10.35)$$

where the plus sign for ε indicates the reversibility of the reference electrode with respect to cations. Generalizing Eqs. (10.34) and (10.35), one can write

$$-d\sigma = q\,d\varepsilon_\pm + \Gamma_\pm d\mu \qquad (10.36)$$

From Eq. (10.36) it follows that

$$-\left(\frac{\partial\sigma}{\partial\mu}\right)_{P,\,T,\,\varepsilon_\mp} = -\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln a}\right)_{P,\,T,\,\varepsilon_\mp} = \Gamma_\pm \qquad (10.37)$$

For solutions containing not one but several electrolytes dissolved in mixed solvents (e.g. in a water-alcohol mixture) the surface excess of a component will be given by the expression

$$-\left(\frac{\partial\sigma}{\partial\mu_i}\right)_{P,\,T,\,\varepsilon_\mp,\,\mu'} = \Gamma_i \qquad (10.38)$$

where the subscript μ' signifies that the electrochemical or chemical potentials of all the components, except the ith component, remain unaltered. Thus, electrocapillary measurements permit one to determine the surface excess of the components of the solution.

It is obvious that from Eq. (10.36) one can obtain the Lippmann equation provided that μ is constant.

Of considerable interest is the effect of capillary-active organic substances on the structure of the double layer and on the shape of electrocapillary curves. This question was first examined by Frumkin in 1926. The essence of Frumkin's theory is as follows.

The adsorption of organic molecules onto an electrode may be regarded as the replacement in the double layer of the water, which possesses a high dielectric constant D_0, by an organic substance with a lower dielectric constant D_1. If this replacement occurs at a potential ε different from the potential of the electrocapillary maximum ε_{ecm}, then the charging of the plates of a double-layer capacitor will change by an amount $(C_0 - C_1)(\varepsilon - \varepsilon_{ecm})$ or $(C_0 - C_1)\varphi$ (if $\varepsilon - \varepsilon_{ecm}$ is designated as φ), where C_0 and C_1 are the specific capacities of the double layer in the initial aqueous solution of an electrolyte and in the same electrolyte containing an organic substance added

[1] Some authors, for example, Grahame, assumed that $\Gamma_{H_2O} = 0$.

in a concentration ensuring its adsorptive saturation. Since usually $D_0 > D_1$ and the size of organic molecules is larger than that of water molecules, then, as follows from the theory of the parallel-plate capacitor, $C_0 > C_1$, and the replacement of water by an organic substance calls for removal of the charge $(C_0 - C_1)\,\varphi$ from the capacitor plates; this requires an energy $(C_0 - C_1)\,\varphi^2$. At the same time the free energy of the capacitor decreases by an amount $0.5\,(C_0 - C_1)\,\varphi^2$. As can be easily seen, the total energy needed to replace a dielectric in a capacitor at a constant plate potential is given by

$$(C_0 - C_1)\,\varphi^2 - \frac{1}{2}(C_0 - C_1)\,\varphi^2 = \frac{1}{2}(C_0 - C_1)\,\varphi^2$$

If we denote by U_0 the gain in energy upon transition of one mole of an organic substance from the bulk of the solution to the uncharged electrode surface (at ε_{ecm}), then at a potential ε this energy gain will be

$$U_\varepsilon = U_0 - \frac{1}{2}(C_0 - C_1)\,\varphi^2\Omega_1$$

where Ω_1 is the surface area of the interface per one mole of the organic substance under conditions of adsorptive saturation. If the organic molecules possess a dipole moment, a potential difference ε_d will arise on their adsorption, which will be numerically equal to the shift in the potential of the electrocapillary maximum caused by addition of an organic substance in a concentration required for adsorptive saturation

$$\varepsilon_d = \varepsilon_{ecm} - \varepsilon_{ecm'}$$

With account taken of this effect, one should write in place of the previous equation:

$$U_\varepsilon = U_0 - \left[\frac{1}{2}(C_0 - C_1)\,\varphi^2 + C_1\varepsilon_d\varphi\right]\Omega_1 \qquad (10.39)$$

From Eq. (10.39) it follows that an organic substance whose adsorption brings about a decrease in the double-layer capacity must be adsorbed most strongly on the electrode surface near the ecm potential, while its desorption from the electrode surface should be expected at higher values of φ when U_ε becomes negative. This conclusion is confirmed by a large number of experimental data.

In its physical meaning Eq. (10.39) is equivalent to a model in which the electric double layer in the presence of adsorbed organic molecules is represented in the form of two parallel-connected capacitors, the space between the plates of one of them containing water molecules and that between the plates of the other being filled with organic molecules. In other words, the charge on the electrode q is additively composed of the charges of the two capacitors, q_0 and q_1:

$$q = q_0\,(1 - \theta) + q_1\theta = C_0\varphi\,(1 - \theta) + C_1\,(\varphi - \varepsilon_d)\,\theta \qquad (10.40)$$

where θ is the surface coverage by the organic substance. This model

consisting of two parallel-plate capacitors is one of the starting points in Frumkin's theory. Another one is associated with the choice of the adsorption isotherm.

To start with, Frumkin assumes that the adsorption of an organic substance obeys Langmuir's equation

$$Bc = \frac{\theta}{1-\theta} \tag{10.41}$$

where c = volume concentration of the organic substance
B = adsorption equilibrium constant, whose dependence on the potential may be written, according to Eq. (10.39) and the Boltzmann distribution law, in the following form

$$B = k \exp\left\{\frac{U_\varepsilon}{RT}\right\} = B_0 \exp\left\{-\frac{\frac{1}{2}(C_0 - C_1)\varphi^2 + C_1 \varepsilon_d \varphi}{RT\Gamma_\infty}\right\} \tag{10.42}$$

where Γ_∞ is the limiting adsorption corresponding to $c \to \infty$ and equal to $1/\Omega$. From Eq. (10.41) and the basic equation of electrocapillarity

$$d\sigma = -q\, d\varphi - RT\Gamma\, d \ln c = -q\, d\varphi - RT\Gamma_\infty \theta d \ln c \tag{10.43}$$

it follows that the decrease of the interfacial tension due to adsorption of an organic substance at a given ε (φ = const) is equal to

$$\Delta\sigma = -RT\Gamma_\infty \ln (1 - \theta) \tag{10.44}$$

Frumkin introduced into Eq. (10.44) an additional term $RT\Gamma_\infty a\theta^2$, which takes into account the attractive interaction between the adsorbed organic molecules

$$\Delta\sigma = -RT\Gamma_\infty[\ln (1 - \theta) + a\theta^2] \tag{10.45}$$

where a is the attractive interaction constant. The combined solution of Eqs. (10.43) and (10.45) after elimination of ε yields a new isotherm

$$Bc = \frac{\theta}{1-\theta} \exp\{-2a\theta\} \tag{10.46}$$

which is now known as the *Frumkin isotherm*. The dependence of B on the electrode potential in this isotherm is given, as before, by Eq. (10.42).

The system of equations (10.40) to (10.46) permits calculation of electrocapillary curves in the presence of different concentrations of an organic substance. First, the dependence of B on φ is determined from Eq. (10.42); then the relation between θ and φ is found from Eq. (10.46) for a given concentration of an organic substance and, finally, the dependence of $\Delta\sigma$ on φ from Eq. (10.45). A comparison made by Frumkin of electrocapillary curves calculated in this

way and obtained experimentally in a $1N$ NaCl solution on addition of different amounts of tertiary amyl alcohol has shown their qualitative agreement.

In recent years Damaskin has developed, on the basis of Frumkin's conceptions, a quantitative theory of differential capacity curves in the presence of an organic substance. The key equation for the double-layer capacity at a constant concentration of an organic substance can be deduced by differentiating Eq. (10.40) with respect to the potential:

$$C = C_0(1-\theta) + C_1\theta - [C_0\varphi + C_1(\varepsilon_d - \varphi)]\left(\frac{\partial\theta}{\partial\varphi}\right)_c \qquad (10.47)$$

Taking logarithm of Eq. (10.46) and differentiating it with respect to the potential at c = const, one obtains:

$$\left(\frac{\partial\theta}{\partial\varphi}\right)_c = \frac{\partial \ln B}{\partial\varphi} \cdot \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \qquad (10.48)$$

At the same time, according to Eq. (10.42),

$$\frac{\partial \ln B}{\partial\varphi} = -\frac{C_0\varphi + C_1(\varepsilon_d - \varphi)}{RT\Gamma_\infty} \qquad (10.49)$$

Substituting Eqs. (10.48) and (10.49) into Eq. (10.47) yields the final equation

$$C = C_0(1-\theta) + C_1\theta + \frac{[C_0\varphi + C_1(\varepsilon_d - \varphi)]^2}{RT\Gamma_\infty} \cdot \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \qquad (10.50)$$

The third term on the right-hand side of Eq. (10.50) describes the characteristic maxima (peaks) on the differential capacity curves in the presence of an organic substance; these curves reflect adsorption-desorption processes. The third term may be neglected near the zero-charge potential, where $(1 - \theta)$ and φ differ little from zero; under these conditions the double-layer capacity will be determined from the formula for two parallel-plate capacitors:

$$C = C_0(1 - \theta) + C_1\theta \qquad (10.51)$$

Since the differential capacity curves are more sensitive to changes in the structure of the electric double layer than electrocapillary curves, a comparison of data calculated from Eq. (10.50) with those obtained experimentally has revealed additional regularities in the adsorption of organic substances on electrodes. For one thing, it has been found that the attraction constant a entering into the Frumkin isotherm (10.46) varies linearly with electrode potential. As shown by Damaskin, this regularity is attributable to the discreteness of the adsorbed dipoles of an organic substance.

A drawback of the theory discussed is that in quantitative calculations one has to borrow the basic quantities for equations from data of electrocapillary and capacity measurements. Numerous

attempts have therefore been made to refine the existing theory or to create a new theory of the double layer in the presence of organic substances.

In 1928 Butler, taking into account the electrical properties of adsorbed particles, deduced the following expression in place of Eq. (10.39):

$$U = U_0 - \left[\frac{1}{2}(\alpha' - \alpha_{H_2O})\varphi^2\gamma + (P' - P_{H_2O})\varphi\gamma v\right] \quad (10.52)$$

where α' and α_{H_2O} = polarizabilities of unit volumes of organic substances and water, respectively

P' and P_{H_2O} = permanent dipole moments of unit volumes of organic substances and water, respectively

v = elementary volume of a dielectric which is transferred from a point of zero field strength to a point of field strength $\psi(\psi = \gamma\varphi)$.

Equation (10.52) contains fewer quantities borrowed from electrocapillary measurements than Eq. (10.39) and therefore permits calculations on the basis of the polarizability and dipole moments of organic substances. Like Eq. (10.39), the Butler equation is in qualitative agreement with experiment and accounts for the decrease in the adsorbability of organic substances with the decreasing distance from the electrocapillary maximum. The Butler theory however should be regarded as one of the versions of Frumkin's theory since their basic premises do not differ substantially.

Other theories of the adsorption of organic substances on electrodes differ from the Frumkin theory either in the form of the equation of state relating interfacial tension to surface excess or in the type of the adsorption isotherm describing the dependence of the surface concentration of an organic substance on its bulk concentration. A further difference consists in that the parameter chosen in the Frumkin-Damaskin theory to characterize the electrical state of an electrode is the potential. According to Parsons, Devanathan and other workers, it must be the surface charge rather than the potential.

Bockris, Blomgren and Conway make use of a modified Langmuir isotherm in which the free energy of adsorption is a decreasing function of the surface excess raised to a power different from unity in contrast to the Frumkin theory, where it is raised to the first power.

Bockris, Devanathan and Muller take into account the competition between the molecules of water and an organic substance for a site in the double layer and emphasize the role of the charge-dependent orientation of water dipoles at the interface.

The Frumkin-Damaskin theory is best applicable to the adsorption of saturated aliphatic molecular compounds with one functional group, which are adsorbed on the electrode in one definite position

The Bockris theory provides the best agreement with experiment in the case of adsorption of organic cations.

It should be noted that the accuracy of present-day experimental data on the adsorption of organic substances, especially on solid electrodes, is not yet high enough for drawing unambiguous conclusions as to which theory and, more specifically, which adsorption isotherm describes most effectively the behaviour of organic substances in the electrode-solution system. Only in some cases can this be asserted with a sufficient degree of certainty. It is evidently necessary to reckon with the fact that the adsorption of aromatic compounds with one functional group or of organic substances with two electrically opposite functional groups occurs differently on positively and negatively charged electrode surfaces, as has been particularly stressed by Antropov and coworkers. The change in the mode of oriented adsorption calls for refining the isotherm equation in order to provide better agreement with experiment.

The theory of the double layer in which all the specific features of the adsorption of organic substances on electrodes are taken into account is still of a semi-quantitative nature; its further development presupposes the improvement of experimental techniques and the availability of more accurate experimental data.

10.3. THE NULL POINTS OF METALS

10.3.1. THE DEFINITION OF THE CONCEPTS "THE POTENTIAL OF AN UNCHARGED SURFACE" AND "THE NULL POINT OF A METAL"; THE CORRELATIVE ("REDUCED") AND "RATIONAL" SCALES OF POTENTIALS

It follows from the Lippmann equation that at the maximum of the electrocapillary curve the charge on the metal surface will be zero [1]. On this basis Ostwald supposed that at the electrocapillary maximum for mercury not only the charge on the metal is equal to zero, but the electrode potential as well. For this reason it is precisely this electrode potential that should be chosen as a basis for the scale of potentials. This scale is called the *absolute* or *Ostwald scale of potentials*. Since the potential of the electrocapillary maximum for mercury in solutions of capillary-active substances is about —0.20 V on the hydrogen scale, it follows, according to Ostwald, that in order to obtain the absolute potential of an electrode one should subtract —0.20 V from the value of its electrode potential on the hydrogen scale (see Table 7.2). The potentials obtained in this way cannot however be considered absolute in the light of present-day conceptions. The potential difference across the electrode-electrolyte interface is

[1] The electrocapillary maximum is therefore also called the *point of zero charge.—Tr.*

not equivalent to the electrode potential but constitutes only a certain part of it. Therefore, if this potential difference is assumed to be equal to zero, one must also take into account the contact potential difference between platinum and another metal (in this particular case, mercury), which is different from zero. Besides, as follows from Eq. (9.23), apart from the term due to ion exchange (which is equal to zero at the electrocapillary maximum), the metal-solution potential difference also includes the term due to orientation of solvent dipoles. There are no grounds to think that this potential difference is zero at the electrocapillary maximum. If Ostwald were right, the electrocapillary maximum would always be at one and the same value of electrode potential irrespective of the solution composition and the nature of the metal. This assumption is not confirmed by experiment. Thus, Gouy found that the potential of the electrocapillary maximum of mercury varies within wide limits depending on the composition of the solution. Other authors, for instance, Luggin (1895), established that the position of the electrocapillary maximum is different if low-melting alloys or liquid amalgams (e. g. lead amalgam) are used instead of mercury. This phenomenon has been studied most thoroughly by Frumkin and his collaborators. According to their data, the ecm potential of gallium is about —0.6 V and that of saturated thallium amalgam about —0.65 V on the hydrogen scale. Following Ostwald, one could take any one of these values, just as the value —0.20 V obtained for mercury, as the "absolute" zero of electrode potential and have three radically different "absolute" potential scales. Thus, it has been shown that the potentials of electrocapillary maxima cannot be used to devise an absolute scale of potentials. But at the same time these potentials, which Frumkin named the null points of metals or the potentials of zero charge (pzc) are of fundamental importance in electrochemistry. On their basis Frumkin suggested a correct solution of the so-called Volta problem, i.e., the buildup of the emf of electrochemical systems and its relation with the contact potential difference between metals.

The terms widely used at present as synonyms for the null point and the potential of the electrocapillary maximum are the *potential of zero charge* and the *potential of an uncharged surface*, which introduces confusion in the electrochemical literature. In order to avoid misunderstanding, Antropov suggested that a distinction should be made between the null point and the potential of an uncharged surface, and each be given a symbol of its own and used according to its meaning; the two terms may be combined into a single general concept, the potential of zero charge. The reason behind this is as follows. The potential of the electrocapillary maximum of mercury (or any other metal) always corresponds to its uncharged surface; this value of potential could be called the uncharged-surface potential (usp) and denoted by $\varepsilon_{q=0}$. The position of the electrocapillary

maximum and the value of the corresponding potential for a given metal and solvent vary widely depending on the nature and concentration of the substances present in the solution. At the same time the partial value of the potential of an uncharged surface obtained for a solution containing no capillary-active particles (except solvent molecules) is a constant characteristic of the given metal and solvent; this partial value of the potential of an uncharged surface should be called the null point and given the symbol ε_N. The null point and the potential of an uncharged surface are interrelated in approximately the same manner as the equilibrium and standard potentials of an electrode. The standard potential is known to be a special case of the equilibrium electrode potential ε_r for a solution with unit activities of all the participants of the electrode reaction. In both cases the composition of the solution must be specified so as to obtain a value which would be a characteristic constant for a particular electrode system.

Suppose we have a cell consisting of a metal immersed in a solution of its ions and a standard hydrogen electrode. The cell emf equal to the electrode potential ε_{LM} of metal M on the arbitrary hydrogen scale may be written, according to Eq. (9.13), in the form:

$$\varepsilon_{LM} = g_{LM} + g_{MPt} + g_{PtL} \tag{10.53}$$

The Galvani potential across the solution-metal interface may be represented, according to Eq. (9.23), as the sum of four terms

$$g_{LM} = g_{LM(q)} + g_{LM(S)} + g^{1)}{}_{LM(dip_1)} + g_{LM(dip_2)} \tag{10.54}$$

where the subscripts q, S, dip_1 and dip_2 refer, respectively, to the potential-determining ions, specifically adsorbed ions, the dipoles of the solvent and the dipoles of any unionized organic substance. If $g_{LM(q)} = 0$, the metal surface has no charge and the electrode potential will correspond to the zero-charge potential

$$\varepsilon_{LM} = g_{LM(S)} + g_{LM(dip_1)} + g_{LM(dip_2)} + g_{MPt} + g_{PtL} = {}_{LM}\varepsilon_{q=0} \tag{10.55}$$

In accordance with what has been said above, the usp potential of a metal depends on the nature of this metal, the reference electrode used, the solvent nature and the solution composition. For the selected metal and solvent the value of ${}_{LM}\varepsilon_{q=0}$ may be different depending on $q_{LM(S)}$ (i.e., the nature and concentration of capillary-active ions) and $q_{LM(dip_2)}$ (i.e., the nature and concentration of capillary-active dipolar molecules). If, however, not only $q_{LM(q)}$ is equal to

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1) In fact, the quantity $g_{LM(dip_1)}$ includes the potential differences due to two dipole layers, one of which is on the solution side and the other, in the surface layer of the metal.

zero, but $q_{LM(S)}$ and $q_{LM(dip_2)}$ as well, i.e., if there are no capillary-active particles in the solution, except the molecules of solvent L, then the following equation should be written in place of Eq. (10.55)

$$\varepsilon_{LM} = {}_{LM}\varepsilon_{q=0} = {}_{N}g_{LM(dip_1)} + g_{MPt} + g_{PtL} \equiv {}_{LM}\varepsilon_{N} \quad (10.56)$$

It can be seen from Eq. (10.56) that this partial value of the usp (i.e., the null point ${}_{LM}\varepsilon_{N}$) must be a constant because it is equal to the sum of three constant quantities.

The null point may also be expressed in terms of the corresponding Volta potentials

$${}_{LM}\varepsilon_{N} = {}_{N}\psi_{LM} + \psi_{PtM} + \psi_{PtL} \quad (10.57)$$

Here the metal-solution Volta potential must be a strictly definite quantity (${}_{N}\psi_{LM}$) corresponding to the difference of external potentials between metal M and the solution, in which the potential of the metal is equal to its null point.

The thus determined null point has been chosen as the zero for the *correlative* (also known as *reduced*) or φ scale of potentials proposed by Antropov (1946-51). The φ potential in the correlative scale is defined as the difference between the potential of an electrode under given conditions and its null point:

$$\varphi = \varepsilon - \varepsilon_{N} \quad (10.58)$$

The two terms on the right-hand side of Eq. (10.58) must naturally be expressed on the same scale (e.g. on the hydrogen scale); the value of the φ potential is independent of the chosen arbitrary or relative scale.

Since the values of ε_{N} are different for different metals (see Tables 10.3 and 10.4), each metal will have its own correlative scale based on its null point. The correlative or φ scale of potentials is thus different from any arbitrary and the absolute scale of potentials. This distinction is clearly seen in comparing the values of standard electrode potentials of some metals on the hydrogen, absolute and reduced scales (Table 10.2).

It can be seen from Table 10.2 that in the hydrogen and absolute scales the arrangement of the metals in order of increasing positive value of standard electrode potential and the differences between any two electrode potentials remain the same. In the correlative scale of potentials the order of arrangement of metals and the differences in the values of their standard electrode potentials are quite different since the physical meaning of the potential in any arbitrary (and in the absolute) scale and in the correlative scale is radically different. While the potentials expressed on the arbitrary scale are referred to a single definite electrode, whose potential is taken as zero, the potential of each electrode in the correlative scale is reckoned

TABLE 10.2

Standard Potentials of Some Metals in Different Scales, V

Electrode	Hydrogen scale	Absolute scale	Correlative scale
Zn^{2+}/Zn	−0.76	−0.76−(−0.20) = −0.56	−0.76−(−0.63) = −0.13
Fe^{2+}/Fe	−0.44	−0.44−(−0.20) = −0.24	−0.44−(+0.0) = −0.44 *
Cd^{2+}/Cd	−0.40	−0.40−(−0.20) = −0.20	−0.40−(−0.7) = +0.3
Tl^{+}/Tl	−0.34	−0.34−(−0.20) = −0.14	−0.34−(−0.8) = +0.46
Hg_2^{2+}/Hg	+0.80	0.80−(−0.20) = +1.00	0.80−(−0.20) = +1.00
Ag^{+}/Ag	+0.80	0.80−(−0.20) = +1.00	0.80−(−0.4) = +1.20 **

* The null point of iron is taken to be not −0.38 V (see Table 9.3) but a more probable value equal to zero.

** The null point of silver is taken to be not the tabulated value −0.76 V but a more probable value equal to −0.4 V.

from its own zero, which is the null point of this electrode metal. It will therefore be wrong to use the φ scale of potentials for solving problems associated with the thermodynamics of electrochemical systems or with electrode equilibrium and to use it instead of the hydrogen scale or the ε scale of potentials. The correlative scale does not enable, for example, determination of the direction of a reaction and the emf of an equilibrium electrochemical system with two electrodes of known φ potential. This task is easily handled with the aid of the ε scale. The potential on the ε scale however yields no information about the charge of the metal surface, the double-layer structure, or the most probable electrical nature of those particles which are preferentially adsorbed on the electrode surface under given conditions. These (and other) data are especially important for understanding nonequilibrium electrode processes and can be obtained by using the φ scale of potentials.

Proceeding from the definition of the φ potential (10.58) and taking into account that the ε potential, which is different from the ε_N potential, is given by the equation

$$\varepsilon_{LM} = g_{LM(q)} + g_{ML(dip_1)} + g_{MPt} + g_{PtL} \qquad (10.59)$$

one can obtain the following expression for the electrode potential on the φ scale [1]:

$$\varphi = \varepsilon - \varepsilon_N = g_{LM(q)} + g_{LM(dip_1)} - {}_N g_{LM(dip_1)} \qquad (10.60)$$

Equation (10.60) allows one to view the electrode potential on the φ scale as a measure of the charge on the metal (the intensitv of the

[1] Equations (10.59) and (10.60) refer to solutions containing no capillary-active substances ($g_{LM(S)} = 0$).

ionic double layer $g_{LM(q)}$) and also as a measure of the variation in orientation of polar solvent molecules at the metal-electrolyte interface upon transition from the null point to the given value of potential (the difference between the quantities $q_{LM\ (dip_1)}$ and $_Nq_{LM\ (dip_1)}$. There are grounds to believe that the orientation of solvent dipoles on a charge-free metal surface depends little on its nature and that the value of $_Ng_{LM\ (dip_1)}$ is approximately the same for all metals in aqueous solutions. Thus, if, for example, for metal *1* and metal *2*

$$\varphi_1 = \varphi_2$$

or

$$g_{LM_1(q)} + g_{LM_1\ (dip_L)} - {}_Ng_{LM\ (dip_L)} = g_{LM_2\ (q)} + g_{LM_2\ (dip_L)} - {}_Ng_{LM\ (dip_L)}$$

then

$$g_{LM_1\ (dip_L)} - {}_Ng_{LM_1\ (dip_L)} = g_{LM_2\ (dip_L)} - {}_Ng_{LM_2\ (dip_L)}$$

since the change of dipole orientation depends only on the electrode charge, and

$$g_{LM_1(q)} = g_{LM_2(q)}$$

The equality of the φ potentials of two or more metals is an indication that the ionic potential differences and the charges on the surfaces of these metals are approximately equal. The same inference can be made if the φ potential is expressed in terms of the corresponding Volta potentials. Knowing the values of the φ potential, one can therefore compare different metals from the viewpoint of their charges and the conditions of adsorption of capillary-active substances on them. If the solution contains capillary-active substances, a study of their adsorption on different electrodes at one and the same φ potential will enable one to ascertain the peculiarities of their specific adsorption on each particular electrode.

In 1947 Grahame, who studied electrocapillary phenomena on mercury, devised a potential scale which he called the *rational scale of potential.* The potential on the rational scale is denoted by ψ′ and given by the equation

$$\psi' = \varepsilon_{nce} - (-0.480) = \varepsilon_{nce} + 0.480 \qquad (10.61)$$

where ε_{nce} is the potential of a mercury electrode with respect to the normal calomel electrode, and the constant value —0.480 corresponds to the potential of the charge-free surface of mercury in solutions of capillary-inactive substances, i.e., to the null point of mercury also referred to the normal calomel electrode.

Obviously, Grahame's rational scale is a special case of Antropov's correlative scale as applied to the mercury electrode. No attempts were made by Grahame to formulate a more general concept of the reduced scale, to extend it to other metals and use it for comparing

charges and the conditions of adsorption on various electrodes. The term "rational potential scale" cannot be considered adequate. Indeed, as pointed out above, the use of a scale based on the null points of metals may prove to be rational in some cases and irrational in others. Moreover, the word "rational", as distinct from "correlative", does not reflect the essence of the scale. And, finally, the rational scale referred only to mercury (the application of this scale as devised by Grahame to other metals would turn it into the Ostwald absolute scale) was proposed after the reduced scale had been put forward. For these reasons we will use henceforward the term "correlative" or "reduced scale of potentials".

It should be noted that in certain cases, alongside the correlative φ scale, the correlative φ' scale may also prove useful, in which the φ' potential is determined from the equation

$$\varphi' = \varepsilon - \varepsilon_{q=0} \tag{10.62}$$

that is, it is reckoned from the potential of the uncharged surface. This scale refers to a single electrocapillary curve whereas the φ scale relates to a given electrode and solvent. Thus, there exists only one φ scale and an infinite multitude of φ' scales for each electrode (say, for a mercury electrode).

10.3.2. METHODS FOR EXPERIMENTAL MEASUREMENT AND CALCULATION OF NULL POINTS

Adsorption phenomena play a very important role in the kinetics of almost all electrode processes. The conditions of adsorption of dissolved substances on the surface of an electrode are largely governed by the charge on this surface, i.e., to a first approximation, by the value of its potential on the correlative scale, a scale based on the null points (the potentials of zero charge) of metals. For this reason, methods of determination of the null points acquire special importance. Several methods are described below.

1. Capillary Electrometer Method. This method can be used to determine the null points (the potentials of zero charge) of liquid metals (e.g. Hg, amalgams, Ga) in contact with electrolyte solutions and also of liquid metals in contact with molten salts. Karpachev and his coworkers have designed a special capillary electrometer to be used for molten electrolytes and determined the null points of a number of metals at temperatures above their melting points.

2. Dropping Mercury Electrode Method. The experiments carried out by Kučera (1912) showed that curves similar to electrocapillary curves can be obtained by using the relation between the weight of a falling-off drop of mercury and its potential. In a dropping mercury electrode drops are continuously formed, falling off from the capillary to the bottom. The drop formation (creation of a new interface bet-

ween mercury and solution) at any potential, except the *ecm* potential, is associated with the injection of charge, i.e., the passage of a current. The potential of a mercury drop at which the current is zero corresponds to the potential of zero charge. The accuracy of this method is lower as compared with the capillary electrometer method, but it is convenient for determining the pzc of electrochemically unstable amalgams.

3. Differential Capacity Method. In dilute electrolytic solutions the potential of the differential capacity minimum of a mercury electrode almost coincides with the electrocapillary maximum obtained for the same solution. Direct measurements of the double-layer capacity on passage of an alternating current were conducted as far back as the 19th century, but the results obtained were not reliable. The application of this method became possible after the works of Proskurnin and Frumkin had been published. These authors showed that with certain conditions being observed (primarily, high purity of the solution and mercury) the capacities measured directly and calculated from electrocapillary curves coincide within experimental errors. Thus the validity of Lippmann's second equation was confirmed. The measurement of the differential capacity of the double layer has turned out to be useful in studying not only the double-layer structure and the adsorption phenomena taking place at the metal-electrolyte interface, but also the kinetics of electrode processes.

The differential capacity method can be employed for determining the pzc of any metal, but in the case of solid metals complications arise, making it difficult to interpret the results obtained. These difficulties are associated with the fact that many solid metals, in particular all the metals of the iron and platinum groups, are capable of adsorbing and occluding considerable amounts of hydrogen and oxygen. This must affect the double-layer differential capacity and its variation with potential. Besides, solid metals usually have surface irregularities: micropores, cracks, dislocations of crystal lattice, etc. For this reason the potential of the differential capacity minimum of a solid metal cannot always be identified with the potential of zero charge. The most reliable data have been obtained for soft metals such as lead, zinc, cadmium and thallium, whose surfaces most closely resemble the mercury surface in their properties.

4. Ionic Adsorption Method. This method consists in determining the sign of the charge of capillary-active ions which are preferentially adsorbed from the solution on the metal surface at a given potential. Anions are primarily adsorbed on positively charged and cations on negatively charged surfaces. If the potential is changed by shifting it in a definite direction, then the point of transition from the excess adsorption of anions to that of cations (or vice versa) will correspond to the potential of zero charge. Excess adsorption of cations or anions

can be established either analytically, by determining the composition of the corresponding solution, or by using a radiotracer technique. The ionic adsorption method is most successfully used for metals with a developed surface (e.g. platinized platinum).

5. Contact Angle Method. This method was proposed by Moller and improved by Frumkin, Kabanov, and others.

A gas bubble or a drop of a liquid immiscible with water is placed on the surface of a metal immersed in a solution. The metal surface

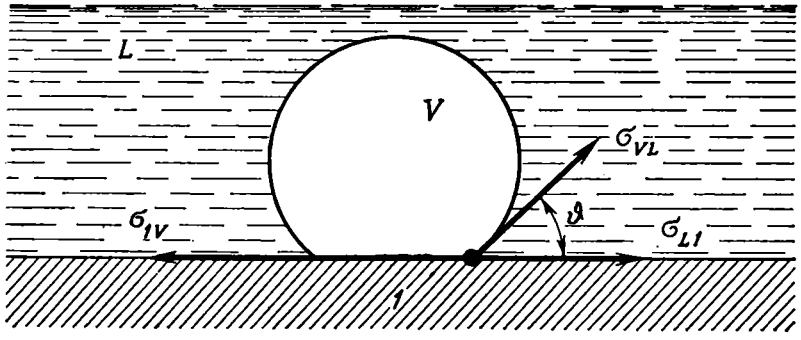

Fig. 10.5. Relation between the contact angle ϑ and the interfacial tension at the metal-solution (σ_{L1}), metal-gas (σ_{1V}) and gas-solution (σ_{VL}) boundaries

is then subjected to polarization and the change of the contact angle ϑ at the boundary between the three phases is measured (Fig. 10.5). It can be seen from Fig. 10.5 that the equilibrium condition will be:

$$\sigma_{1V} = \sigma_{L1} + \sigma_{VL} \cos \vartheta$$

where σ is the interfacial tension between the two phases. After rearranging,

$$\cos \vartheta = \frac{\sigma_{1V} - \sigma_{L1}}{\sigma_{VL}} \qquad (10.63)$$

A curve of contact angle ϑ versus potential ε is similar to an electrocapillary curve—its maximum corresponds to the potential of zero charge. This shape of the ϑ vs. ε curve is probably explained by the fact that σ_{VL} is independent of potential, σ_{1V} changes very slightly with potential and all changes in the contact angle should be ascribed to σ_{L1}. The accuracy of this method is inferior to that of the electrocapillary method. It can, however, be used for determining the pzc of metals with a smooth surface.

Fischer and Morlos recently used a version of this method based on the relation between the contact angle ϑ and the height h of the capillary rise of a liquid on a metal plate:

$$\sin \vartheta = 1 - \rho\, gh^2/2\sigma$$

where ρ = density of the liquid
g = acceleration due to gravity
σ = interfacial tension.

Experiments carried out with an amalgamated gold plate have shown that the minimum of the curve for the height of the liquid against the plate potential is close to the potential of zero charge found for the corresponding solution, and its variation with the solution composition agrees with data of electrocapillary measurements.

6. Surface Hardness Method (The Pendulum Method). This method was proposed by Rehbinder and Wenstrom (1945-49). It consists in measuring the logarithmic decrement of the oscillations of a pendulum in contact with a metal surface through a drop of an electrolyte solution. The logarithmic decrement of the oscillations was plotted versus the metal-solution potential difference.

According to Rehbinder and Wenstrom, the decrement of the oscillations is associated with the deformation of the surface and the penetration of the pendulum into the bulk of the metal. The higher the free energy of the metal-solution interface, the greater the amount of work required to create a fresh surface and the slower the rate of deformation; hence more time is needed now for the same relative decrement of the oscillations to be attained. The maximum surface hardness coincides with the maximum surface energy and they both must be observed at the potential of zero charge. The Rehbinder-Wenstrom method was modified by Bockris and Parry-Jones (1953), who suggested that the position of the potential of zero charge should be determined from the minimum surface friction. The determination of the pzc by these two methods requires high experimental skill, which limits their practical application.

7. Vibrating Boundary Method. The method, which was proposed by Watanabe in 1963, consists in the following. The surface of a liquid metal charged to a definite potential is made to vibrate in the solution under study by means of a mechanical vibrator. The surface area of the interface between the metal and the solution changes at a definite frequency and the electric double layer generates an alternating charging-discharging current on the surface. At the potential of zero charge the magnitude of the alternating current produced will be minimal (in the limit equal to zero). A shortcoming of the method is that the measurements involve the passage of a current through the system. This lowers the sensitivity of the method, especially in dilute solutions, because of a voltage drop caused by the solution resistance.

Mintz and coworkers (1967) succeeded in increasing the sensitivity of the method by inserting a controlling resistance into the charging-discharging current circuit. This enabled measurements to be made in slightly more dilute solutions.

A modified version of this method was described by Yu. Gerasimenko, M. Gerasimenko, and L. Antropov (1971). The electric double layer on the vibrating metal surface generates an alternating voltage (not an alternating current) having the same wave characteristic as mechanical vibration. The magnitude of the alternating voltage depends on the specified potential on the metal and tends to zero as this potential approaches the zero-charge potential. This version of the vibrating boundary method provides sufficient accuracy and can be used for measurements in very dilute solutions.

Other Experimental Methods for Determining the Potential of Zero Charge. The values of the pzc of metals can also be obtained by means of a number of other methods. One of these is based on the fact that under definite conditions the zero value of the electrokinetic potential corresponds to an uncharged metal surface. The magnitude of the electrode potential at which the electrophoretic (or electroosmotic) velocity is equal to zero may be identified here with the potential of zero charge. For the same purpose use can be made of the results of experiments with deflection of a thin wire in an electric field; in this case the potential of zero charge may be identified with the potential of the wire at which it ceases to deflect. Further, an approximate value of the potential of zero charge can be obtained from data on the effect of salts on the kinetics of hydrogen evolution at the cathode. A new method for determining the pzc has been proposed by Derjaguin, Kabanov, and Birintseva (1960). The position of the pzc is determined by measuring the repulsive forces arising when two equally polarized metallic wires are brought close together (the *crossed fibre method*). The potential at which the repulsive force is at its minimum is taken as the potential of zero charge.

An interesting method has been devised by Gokhshtein. The method in essence is as follows. An electrode in contact with a solution is attached to a piezoelectric cell and charged at a definite frequency and rate to a potential kept within two volts. The range of variation of the potential remains constant whatever its value. Oscillations of the surface tension arising at the electrode-solution interface are recorded by the piezoelectric cell. As can be seen from the electrocapillary curves, one and the same amplitude of oscillations of the potential causes the surface tension to oscillate at different amplitudes; as the electrode potential approaches the electrocapillary maximum, where the surface tension is almost independent of the potential (at sufficiently small variations of the latter), the oscillations of the surface tension fall sharply. The minimum of the curve of the surface tension amplitude against the potential (its range being specified) must therefore correspond to the potential of zero charge of the electrode. The first experimental data obtained by Gokhshtein support this assumption.

The values of the pzc determined by the methods described above are presented in Table 10.3. When using the tabulated values of the pzc it is necessary to remember that the degree of accuracy largely depends on the method used for their determination. The most accurate results have been obtained by the capillary-electrometer and dropping-electrode methods. The null points of metals (except mercury) found by different methods coincide with an accuracy up to 0.1 V.

A direct comparison of the pzc of metals in solutions and in molten electrolytes is impossible because of the absence of a single scale of electrode potentials for aqueous solutions and molten media. They can nevertheless be compared assuming that the null point of some metal is the same both in solution and in molten electrolytes. Such a comparison has been made on the assumption that the null points of mercury in solution and in melts are equal (Frumkin, Antropov). The choice of mercury is dictated by the fact that it is in the liquid state when in contact with aqueous solutions as well as molten salts. Besides, the null point of mercury in aqueous solutions has been determined with the greatest accuracy. With this assumption made, the null points of metals in molten electrolytes (with respect to the reference electrode: lead and a eutectic of lithium chloride and potassium chloride) can be converted to the hydrogen scale by adding a constant value (equal to —0.1 V) to the values given in Table 10.2. A still better agreement between the two rows of null points can be provided if their values for molten electrolytes and solutions are assumed to be equal not for mercury, whose null point in a molten electrolyte is determined with insufficient accuracy, but for lead. This is what was recently done by Leikis and Ukshe. Thus, the null points of all metals in two different solvents differ by a certain constant value.

The results obtained by conversion are given in Table 10.5, where they are compared with the most probable values of the null points in solutions and also with calculated values. The agreement between the three rows of null points thus obtained is quite satisfactory.

Theoretical Calculation of Null Points. One cannot say with sufficient certainty (except for mercury) that the values listed in Tables 10.3 and 10.4 are really the null points of the metals and not their potentials of zero charge. This uncertainty arises from the fact that ions which are not surface-active at the mercury-water interface are capable of being specifically adsorbed on the surfaces of other metals. Therefore, electrolytes in which, in the case of a mercury electrode, conditions are observed under which the values of pzc obtained are equal or very close to the null point of mercury in a given solvent, may prove to be surface-active for other metals, and the experimentally determined potentials of zero charge will differ from the null points. In this connection it would be very interesting to try and calculate the null points of metals theoretically. The basis

TABLE 10.3

Experimental Zero-Charge Potentials of Metals in Aqueous Solutions (on the Hydrogen Scale)

Metal	Solution	Method	ε_N, V
Te	1*N* Na_2SO_4	Surface hardness (or pendulum)	+0.60 *
Pt (hydrogen atmosphere)	1*N* Na_2SO_4, 0.01*N* H_2SO_4	Adsorption	+0.11
			+0.15
		Contact angle	+0.27
		Crossed fibres	+0.2 *
C (activated carbon)	1*N* Na_2SO_4, 1*N* H_2SO_4	Adsorption	−0.03 *
Ni	0.001*N* H_2SO_4	Hydrogen overpotential	−0.06
C (graphite)	0.05*N* NaCl	Surface hardness (pendulum)	−0.07 *
Cu	Acidified salt solutions	Adsorption	−0.06
		Contact angle	−0.11
		Surface hardness	−0.26
Ag	1*N* KNO_3 dil. $AgNO_3$	Adsorption	+0.05
	1*N* KNO_3 dil. $AgNO_3$	Contact angle	−0.02
	0.002*N* $AgNO_3$	Differential capacity	−0.70 *
Hg	Dilute solutions	Various methods	−0.19* to −0.21
Sn	0.1*N* Na_2SO_4, 0.01*N* H_2SO_4	Surface hardness	−0.24 *
Fe	0.001*N* H_2SO_4	Differential capacity and hydrogen overpotential	−0.37
Cr	0.01*N* NaOH	Contact angle	−0.45
Ga	1.0*N* KCl, 0.1*N* HCl	Capillary electrometer	−0.62 *
Zn	1*N* Na_2SO_4	Surface hardness	−0.62 *
Pb	0.1*N* Na_2SO_4	Surface hardness	−0.56 to −0.60
	Dilute KCl, HCl and H_2SO_4 solutions	Differential capacity	−0.65 to −0.69 *
Cd	Dilute solutions of electrolytes, 0.005*N* KCl	Surface hardness	−0.7 *
		Differential capacity	−0.89
Tl	1*N* Na_2SO_4	Surface hardness	−0.66 to −0.69
	Dilute solutions of electrolytes	Differential capacity	−0.79 *
Tl (Hg), saturated amalgam	1*N* Na_2SO_4	Capillary electrometer	−0.65 *
Na (Hg) 1g-atom/litre	0.1*N* LiCl, NaOH	Dropping mercury electrode	−1.92 *

* Probable values of null points.

TABLE 10.4

The Zero-Charge Potentials of Molten Metals *

Metal	ε_N, V	Molten electrolyte	t, °C	Method
Te	+0.60	KCl + LiCl eutectic	550	Capillary electrometer
Sb	+0.10	KCl + LiCl eutectic	750	Capillary electrometer
Sb	+0.30	Equimolecular melt of KCl + NaCl	700	Differential capacity
Hg	−0.10	KCl + LiCl eutectic	420	Capillary electrometer
Sn	−0.23	KCl + LiCl eutectic	450	Capillary electrometer
Sn	−0.12	Equimolecular melt of KCl + NaCl	700	Differential capacity
Bi	−0.30	KCl + LiCl eutectic	450	Capillary electrometer
Bi	−0.12	Equimolecular melt of KCl + NaCl	700	Differential capacity
Al	−0.30	KCl + LiCl eutectic	750	Capillary electrometer
Ag	−0.30	KCl + LiCl eutectic	1050	Capillary electrometer
Ga	−0.40	KCl + LiCl eutectic	450	Capillary electrometer
Pb	−0.47	KCl + LiCl eutectic	450	Capillary electrometer
Pb	−0.35	Equimolecular melt of KCl + NaCl	700	Differential capacity
Zn	−0.55	KCl + LiCl eutectic	450	Capillary electrometer
Cd	−0.63	KCl + LiCl eutectic	450	Capillary electrometer
Cd	−0.60	Equimolecular melt of KCl + NaCl	700	Differential capacity
Tl	−0.64	KCl + LiCl eutectic	420	Capillary electrometer
Tl	−0.67	Equimolecular melt of KCl + NaCl	700	Differential capacity
In	−0.52	KCl + LiCl eutectic	450	Capillary electrometer

* The pzc values are given with respect to a reference electrode – molten lead and KCl–LiCl eutectic.

for such calculations was given by Frumkin. He assumed that the difference between the null points of two metals must be approximately equal to the Volta potential between them:

$$ {}_1\varepsilon_N - {}_2\varepsilon_N = \psi_{1,2} = \frac{\omega_1^e - \omega_2^e}{F} \qquad (10.64) $$

TABLE 10.5

Comparison of the Null Points of Some Metals Measured in Aqueous Solutions and in Molten Electrolytes and Calculated by Eq. (10.66) from Electronic Work Function

Null Point	Ag	Al	Cd	Fe	Ga	Hg	Pb	Pt	Sn	Tl	Zn
$M\varepsilon_N$ in aqueous solutions, V	−0.02 −0.70	— —	−0.7* −0.89	±0.0 −0.37	−0.62*	−0.2	−0.56 −0.69*	+0.2*	−0.24	−0.66 −0.79*	−0.62
$M\varepsilon_N$ in molten electrolytes (converted), V	−0.40*	0.40*	−0.60 −0.73*	—	−0.50	−0.2	−0.45 −0.57		−0.22 −0.39*	−0.74 −0.77*	−0.65*
$M\varepsilon_N$ from work function, V	−0.40*	−0.40*	−0.7	−0.40 ±0.0	−0.6*	−0.2	−0.7*	+0.2*	−0.4*	−0.8*	−0.5*
ω_M^e, eV	4.3	4.3	4.0	4.3 4.7	4.1	4.5	4.0	4.9	4.3	3.9	4.2

* Probable values of null points.

Equation (10.64) has been confirmed qualitatively in the experimental works of Karpachev and coworkers devoted to the null points of molten metals. All the methods proposed for calculating null points (by Vasenin, Antropov, Delahay and Ruetschi, Levin, Novakovsky and Ukshe, and others) make use, directly or indirectly, of Eq. (10.64). The approximate nature of this equation was noted by Frumkin, who expressed some ideas about possible causes of deviation of the relation between the null points and contact potentials from linearity. The conditions under which Eq. (10.64) must be fulfilled have been discussed by Parsons and Antropov. It is impossible to substantiate theoretically the necessity to observe these conditions, and therefore the validity of Eq. (10.64) and also the usefulness of the methods suggested for calculating null points can be proved or refuted only by experiment.

Equation (10.64) can be transformed by solving it for the null point of metal 1:

$$_1\varepsilon_N = {}_2\varepsilon_N + \frac{\omega_1^e - \omega_2^e}{F} \qquad (10.65)$$

For calculations with the aid of Eq. (10.65) it is necessary to choose a certain standard metal 2. Mercury is the best choice because its electronic work function and null point have been determined with least error; they are, respectively, 4.52 eV and —0.19 V.

Substitution of these values of $_2\varepsilon_N$ and ω_2^e into Eq. (10.65) gives

$$_M\varepsilon_N = \frac{\omega_M^e}{F} - 4.52 - 0.19 = \frac{\omega_M^e}{F} - 4.71 \approx \frac{\omega_M^e}{F} - 4.7 \qquad (10.66)$$

Equation (10.66) permits calculating the null point of any metal if its electronic work function is known. The accuracy of these calculations depends, apart from the validity of starting premises, on how accurately the work functions have been determined. The dependence corresponding to Eq. (10.66) is shown graphically in Fig. 10.6, from which it can be seen that the deviation of experimental points from the theoretical straight line is in most cases within experimental errors. Thus, by using Eq. (10.66) it is possible to calculate the null points of metals with an accuracy close to that provided by most direct measurements (± 0.1 V).

The null points of a number of metals have been calculated from Eq. (10.66) on the basis of the values of work function indicated in Table 9.1. The calculated values of null points are given in Table 10.5.

Recently Antropov introduced the concept of the theoretical metal-solvent null point $_{M/L}\varepsilon_N^T$, which is defined as a special case of the equilibrium metal-solution potential, when the charges on the free surfaces of a metal and a solution are equal in magnitude and so are

their external potentials ψ_M and ψ_L:

$$|\psi_M = \psi_L|\varepsilon_N^T \tag{10.67}$$

With this condition, from the general equation for the equilibrium electrode potential on the hydrogen scale

$$_{M/L}\varepsilon_N^T = \frac{1}{zF}\left(z\omega_M^e + \omega_M^{M^{2+}} - \omega_L^{M^{2+}} + z\omega_L^{H^+} - \frac{z}{2}D_{H_2} - zI_{H^+}\right) \tag{10.68}$$

where ω = work function
D_{H_2} = dissociation energy
I_{H^+} = energy of hydrogen ionization
it follows that

$$_{M/L}\varepsilon_N^T = \frac{1}{zF}\left(z\omega_M^e + zA_{ch(L^0)}^{H^+} - zF\chi_{L^0} - \frac{z}{2}D_{H_2} - zI_{H^+}\right) \tag{10.69}$$

The dissociation energy of hydrogen molecules and the ionization energy of its atoms are independent of the nature of the metal and the

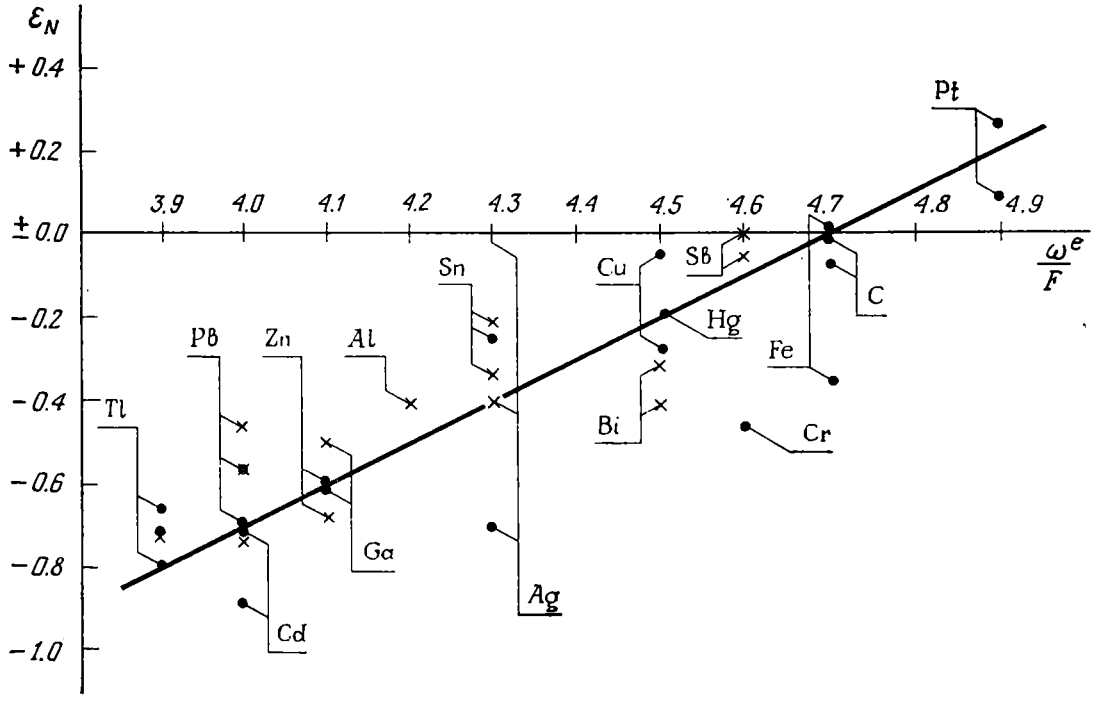

Fig. 10.6. Relation between the null points of metals (ε_N) and the electronic work functions (ω^e):

●—null points in solutions; ×—null points in molten electrolytes recalculated on the assumption that for mercury $\varepsilon_{N(soln)} = \varepsilon_{N(melt)} = -0.2$V

solvent and are equal to 4.22 and 13.60 eV, respectively. Consequently,

$$_{M/L}\varepsilon_N^T = \frac{1}{zF}(z\omega_M^e + zA_{ch(L^0)}^{H^+} - zF\chi_{L^0} - 15.71) \tag{10.70}$$

Equation (10.70) shows that the difference between the null points of two metals M_1 and M_2 in the same solvent L, i.e., the quantity

$$_{M_1/L}\varepsilon_N^T - {}_{M_2/L}\varepsilon_N^T = \frac{1}{F}(\omega_{M_1}^e - \omega_{M_2}^e) = \Delta\psi_{M_1M_2} \qquad (10.71)$$

is equal to the difference in the electronic work functions of these metals and is independent of the solvent nature. Equation (10.71) coincides with the Frumkin formula (10.64), which thus refers to null points rather than to the potentials of zero charge and is fulfilled only when the assumption of the equality $\psi_M = \psi_L$ [i.e., Eq.(10.67)] is valid. From Eq. (10.70) it follows also that the null point of any metal M in two solvents L_1 and L_2 is not a function of the metal's nature. Indeed,

$$_{M/L_1}\varepsilon_N^T - {}_{M/L_2}\varepsilon_N^T = \frac{1}{F}(A_{r(L_1)}^{H^+} - A_{r(L_2)}^{H^+}) = \Delta\psi_{L_1L_2} \qquad (10.72)$$

that is, the difference between the null points of one and the same metal in two solvents corresponds to the Volta potential between these solvents.

Because of the lack of experimental data the calculation of null points by Eq. (10.70) can be carried out only for aqueous solutions. In this case, according to Izmailov and also to Conway, the quantity $A_{ch\,(H^+)}^{H_2O} = 258$ kcal/g-ion $= 11.19$ eV/g-ion and hence

$$_{M/H_2O}\varepsilon_N = \frac{1}{F}\omega_e^M - \chi^{H_2O} - 4.52 \qquad (10.73)$$

The magnitude of the surface potential at the water-air boundary is 0.17 V according to the indirect data of Izmailov; according to Frumkin, it must lie between 0.1 and 0.2 V, closer to 0.2 V. If the value given by Izmailov is used, i.e., if it is assumed that $\chi^{H_2O} = 0.17$ V, then

$$_{M/H_2O}\varepsilon_N = \frac{1}{F}\omega_e^M - 4.52 - 0.17 = \frac{1}{F}\omega_e^M - 4.69 \simeq \frac{1}{F}\omega_e^M - 4.7 \qquad (10.74)$$

which coincides with Eq. (10.66).

At present it cannot be stated with a sufficient degree of certainty that the null point calculated theoretically on the basis of the assumption (10.69) corresponds both in physical meaning and in magnitude to the experimental null point. Nevertheless, the similarity of Eqs. (10.66) and (10.71), in which different initial values were used, can hardly be regarded as casual. Besides, Eq. (10.72) leads to the conclusion that the differences in the null points are independent of the solvent nature, which agrees with the data obtained so far on the null points in aqueous solutions and in molten salts. And, finally, it should be noted that Eq. (10.70) can be used to determine the surface potential χ^L (or χ^{H_2O} for aqueous solutions) which, as follows from the substitution of the values of ε_N and ω^e for mercury into Eq. (10.71), must be equal to 0.19 V. This value of χ^{H_2O} is only slightly different from the most probable value of the surface potential at the water-vacuum boundary found by other methods.

CHAPTER II

The Structure of the Electric Double Layer at the Electrode-Electrolyte Interface

The study of electrokinetic and electrocapillary phenomena has yielded definite experimental regularities. The theory of the double-layer structure at the metal-electrolyte interface is the basis for interpretation of these regularities. Experimental facts may serve at the same time as a criterion of the validity of the various conceptions of the double-layer structure. The most important results obtained in studying electrokinetic and electrocapillary phenomena may be summarized as follows.

1. Apart from the total metal-electrolyte potential difference g_{LM}, which is a concentration-dependent component of the electrode potential ε_{LM}, there also exists the electrokinetic or zeta (ζ) potential differing from the total potential difference. The zeta potential is usually smaller in absolute value than g_{LM} or ε_{LM} and its dependence on the solution composition is more sophisticated. In most cases, with increasing concentration of the electrolyte the zeta potential diminishes, tending to zero, provided that the solution contains no surface-active ions. When the concentration of the solution changes, a reversal of the sign of the ζ potential may result, though the sign of the ε potential remains the same. This reversal of the sign of the ζ potential and the associated recharging of the metal surface is observed in the presence of surface-active (or capillary-active) and polyvalent ions.

2. The differential capacity calculated from electrocapillary curves or measured directly is a function of the electrode potential. It is at its minimum in the region of potentials adjacent to the zero-charge potential of mercury in a given solution. For solutions containing no capillary-active substances the magnitude of capacitance at the electrocapillary maximum decreases regularly as the solution is diluted. The capacitance on the negative (descending) branch of the electrocapillary curve is usually lower than on the positive (ascending) branch; in many electrolyte solutions it varies slightly with potential, from 15 to 30 $\mu F/cm^2$.

Various attempts have been made to build up realistic conceptions of the double-layer structure at the metal-solution interface; the principal theories of the double-layer structure are discussed below.

11.1. THE PARALLEL-PLATE CONDENSER THEORY OF THE DOUBLE LAYER

The first quantitative theory of the double-layer structure at the metal-solution interface is usually associated with the name of Helmholtz. According to Helmholtz (1853), the double layer may be regarded as an equivalent of an electrical parallel-plate condenser, one plate of which coincides with the plane passing through the surface charges in the metal and the other with the plane connecting the centres of the ions residing in the solution but attracted to the

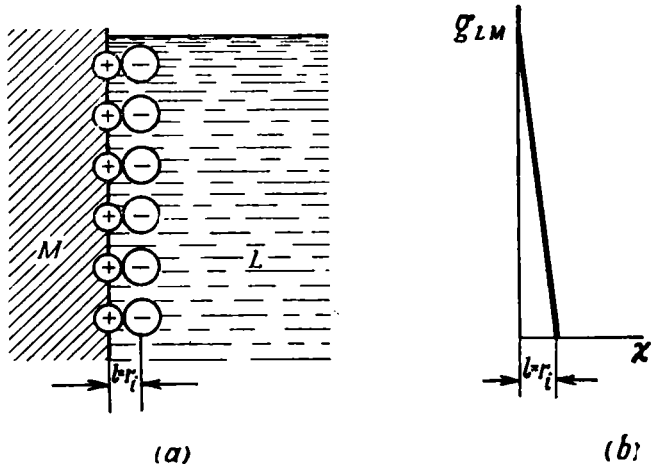

Fig. 11.1. The Helmholtz model of the double layer: *a*—molecular picture; *b*—variation of potential with distance from the metal-solution interface

metal surface by electrostatic forces (Fig. 11.1). The thickness of the double layer l (i.e., the distance between the condenser plates) is taken to be equal to the ionic radius r_i. By the law of electroneutrality, which also holds for the phase boundary, the number of ions drawn to the metal surface must be such as to precisely compensate the surface charges of the metal, i.e.,

$$q_M = -q_L \tag{11.1}$$

if q_M and q_L are surface charges per unit area (or charge densities) on the metal side and the solution side of the interface.

From the familiar equation for the parallel-plate condenser it follows that the charge density is directly proportional to the metal-solution potential difference due to a complete double layer:

$$q = Cg_{LM(q)} \tag{11.2}$$

where C is the capacity (capacitance) of the double layer.

The model of the electrical double layer in accord with these simplest conceptions implies two possible values of the zeta potential.

If it is assumed that all the charges in the solution are capable of moving together with the liquid or are not entrained by a solid moving relative to the liquid, the zeta potential will then coincide in magnitude with the g_{LM} potential and its variation with electrolyte concentration must obey the Nernst formula. But if the charges present in the solution are bound strongly with the solid and move together with it (when the liquid and the solid move relative to each other), the ζ potential will always be equal to zero. None of these corollaries of the Helmholtz theory is consistent with the experimentally established relation between the ε (or g_{LM}) and ζ potentials or with the experimental concentration dependence of the ζ potential if it is not assumed that the latter may be equal to zero in very concentrated electrolyte solutions or at a definite solution composition corresponding to the isoelectric point. Also, the Helmholtz theory does not explain why the surface charge density on the metal surface changes at a given value of the ε potential in the presence of capillary-active substances. At the same time the parallel-plate condenser model of the double layer allows one to obtain double-layer capacities consistent with experiment and also a physically plausible double-layer thickness based on experimental values of the capacity. For a double layer having the properties of a parallel-plate condenser one can write

$$q = \frac{D}{4\pi l} g_{LM(q)} \tag{11.3}$$

where

$$\frac{D}{4\pi l} = C \tag{11.4}$$

D being equal to the dielectric constant (permittivity) of the medium filling the space between the plates of the condenser.

In solutions containing no surface-active substances the capacity of a mercury electrode on the negative (descending) branch of the electrocapillary curve is on the average 20 $\mu F/cm^2$. Since

$$1 \text{ faraday} = \frac{1 \text{ coulomb} \times 3 \times 10^9}{1 \text{ volt} \times \frac{1}{300}} = 9 \times 10^{11} \text{ esu of capacity}$$

then $1\ \mu F = 1 \times 10^{-6} F = 9 \times 10^5$ esu of capacity and hence

$$\frac{l}{D} = \frac{1}{4\pi C} \approx 0.4 \times 10^{-8} \text{ cm}$$

If we assume that the solvent in the double layer is in a state close to dielectric saturation, the dielectric constant may be taken to be close to unity (from 1 to 5). The thickness of the double layer will then be of the order of 10^{-8} cm, which corresponds to the usual ionic radii. Similarly, by substituting the value of ionic radius

($n \times 10^{-8}$ cm) for l into Eq. (11.4) and assuming that D lies between 1 and 5, one can obtain double-layer capacities coinciding with experimental values. However Eq. (11.3) does not account for the experimentally observed change in the capacity with potential and with ion concentration in solution. The Helmholtz theory is thus incapable of providing a satisfactory interpretation of the basic experimental regularities associated with the double-layer structure and cannot therefore be considered perfect. In many cases, however, especially in the region of concentrated electrolyte solutions, this theory leads to conclusions which agree with experiment. Hence, the Helmholtz theory reflects more or less correctly the true structure of the electrical double layer.

11.2. THE DIFFUSE-LAYER THEORY

The Helmholtz theory does not take into account that the properties of the double layer change with electrolyte concentration and temperature. Gouy (1910) and Chapman (1913) made an attempt to eliminate this weakness of the Helmholtz theory by relating the charge density in the double layer to the solution composition. They noted that the strictly fixed array of ions postulated in the parallel-plate model is in fact impossible because, apart from the electrostatic forces arising between the metal and the ions, the latter are also acted on by the forces of thermal molecular motion. Under the combined effect of these forces the ions in solution are distributed diffusely relative to the metal surface, the space charge density decreasing with distance from it just as the density of the atmosphere changes with height. For this structure of the double layer one cannot make use of the formula for a parallel-plate condenser to express the relation between the potential and the charge density. In accordance with the law of electroneutrality one can write:

$$q_M = -q_L$$

i.e., the net charge density q_L on the electrode must be equal in magnitude and opposite in sign to the net charge density q_L on the solution side. But in order to find the value of q_L as a function of potential some definite assumptions must be made on the law of its variation with distance from the electrode. Gouy and Chapman maintain that the ions may be viewed as material points having no volume but possessing a definite charge and that their distribution in the field of the charge smeared uniformly over the electrode surface obeys the Boltzmann formula (Fig. 11.2). The value of q_L is determined in this case by summation of all the excess charges of the ions (positive for a negatively charged and negative for a positively charged metal surface) present in a liquid column normal to the electrode surface and having a cross-sectional area of 1 cm^2.

The magnitude of the surface charge per unit area on the solution side of the interface is found in the same way as the charge density of the ionic atmosphere in calculations of the ionic activity coefficient by the first approximation of the Debye-Hückel theory [1]. The starting points in both cases are the Boltzmann and Poisson

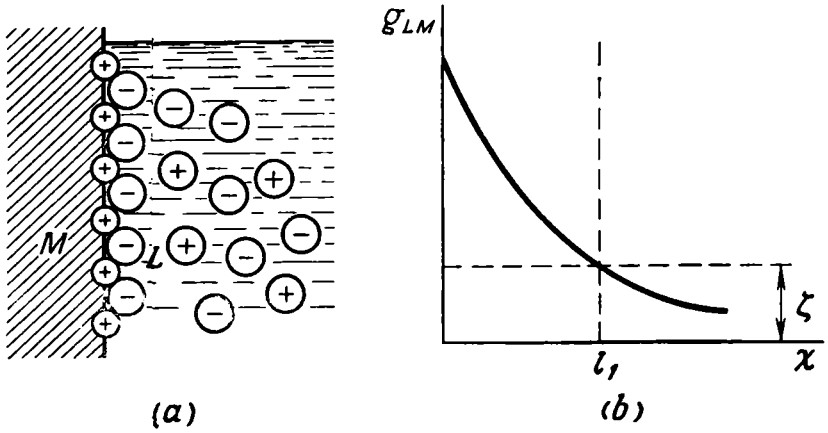

Fig. 11.2. The Gouy-Chapman diffuse-charge model of the double layer:
a—molecular picture; *b*—variation of potential with distance from the metal-solution interface

equations. In determining q_L, one coordinate is sufficient, namely the distance from the electrode surface into the bulk of the solution. In this particular case Poisson's equation (2.31) is simplified to

$$\nabla^2\psi = \frac{d^2\psi}{dl^2} = -\frac{4\pi}{D} q_L \tag{11.5}$$

One can therefore write for q_L

$$q_L = \sqrt{\frac{DRTc}{2\pi}} \left(e^{\frac{Fg_{LM(q)}}{2RT}} - e^{\frac{Fg_{LM(q)}}{2RT}}\right) \tag{11.6}$$

Equation (11.6) refers to a completely dissociated uni-univalent binary electrolyte ($\alpha = 1$, $c_+ = c_- = c$) which obeys the laws for ideal gas systems.

The concept of the zeta potential does not figure in the diffuse-double-layer theory and its value therefore does not appear in Eq. (11.6). Nevertheless, this theory is in better agreement with the regularities established in studying electrokinetic phenomena than the Helmholtz theory. Indeed, if one assumes that beyond a certain distance, say l_1, the ions are no longer bound strongly with the electrode surface during the relative motion of the solid and liquid phases, the value of the potential corresponding to this distance (see Fig. 11.2) may then be identified with the zeta potential. By

[1] The works of Gouy and Chapman were published before the Debye-Hückel theory and served as a stimulus for the development of this theory.

the Gouy-Chapman theory and also according to an analysis of electrokinetic phenomena, the zeta potential is in fact different from both the total potential difference q_{LM} and the electrode potential ε, ζ being smaller than g_{LM}. If the concentration of the solution increases, the charge density q_L will also increase simultaneously. The forces of attraction between the metal surface and the oppositely charged ions become stronger, while the degree of diffusion and the

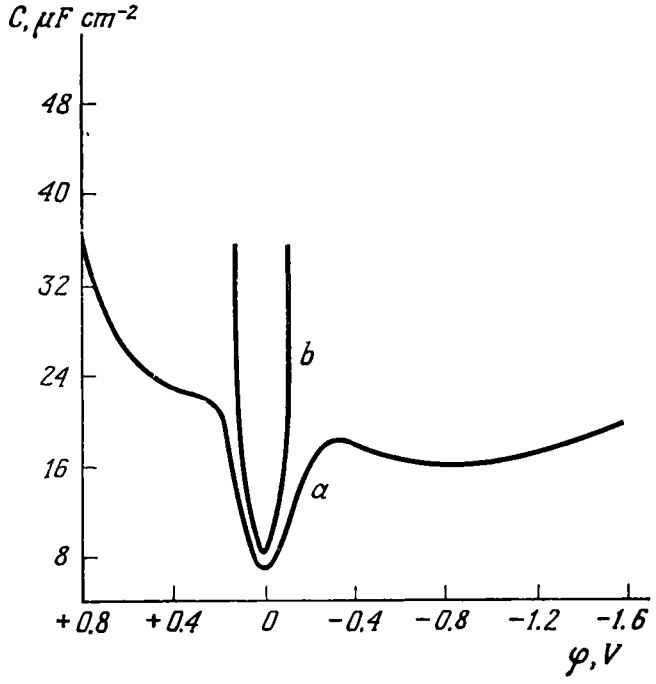

Fig. 11.3. Comparing the experimental (*a*) and theoretical (*b*) (according to the Gouy-Chapman theory) curves of differential capacity for 0.001*N* NaF

magnitude of the zeta potential decrease, which agrees well with experimental data. The Gouy-Chapman theory however does not account for such experimental facts as the reversal of the sign of the ζ potential and the recharging of the metal surface. According to this theory, the sign of the ζ potential must always be identical with that of the total potential difference across the metal-solution interface.

The value of the capacity can be obtained by differentiating both sides of Eq. (11.6) with respect to the potential $g_{LM(q)}$, which may be replaced, with a certain degree of approximation, by the electrode potential on the correlative φ scale.

Figure 11.3 compares the experimental curve of the variation of the double-layer capacity with the φ potential for a mercury electrode in an aqueous 0.001*N* NaF solution, obtained by Grahame, with the theoretical curve calculated for the same solution from Eq. (11.6)

after its differentiation with respect to the φ potential. Neither the course of the theoretical curve with potential nor the absolute values of capacity agree with experimental data [1]. The discrepancy becomes still more pronounced for concentrated solutions. The calculated capacities are several times, even several tens of times, as high as the experimental values. For example, the experimental values of the capacity in 1.0 *N* solutions of NaF and KCl at the point of zero charge (the electrocapillary maximum) are, respectively, 25.7 and 39.0 μF/cm², while calculations yield a value of 228.0 μF/cm². This discrepancy arises from the neglect in the Gouy-Chapman theory of the volume of ions, these being regarded as point charges. As a result, in the diffuse-layer model nothing prevents the ions from getting infinitely close to the metal surface. The solution portion of the double layer may prove to be localized, despite its diffuse structure, in a very thin lamina of thickness considerably smaller than the ionic radius. According to Eq. (11.4) the capacity is inversely proportional to the double-layer thickness. The possible compression of the diffuse layer to a thickness smaller than the ionic radius results in overstated values of the capacity. Thus, the Gouy-Chapman model, although providing a better explanation of electrokinetic phenomena than the Helmholtz theory, proves less efficient when applied to quantitative calculations of the double-layer capacity.

11.3. THE ADSORPTION THEORY OF THE DOUBLE LAYER

The Gouy-Chapman theory is best justified where the Helmholtz theory is found to be inapplicable, and, conversely, where the diffuse-charge model yields wrong results, the parallel-plate model provides a better agreement with experiment. Hence, the structure of the electrical double layer must be described by a certain combination of the models proposed by Helmholtz and Gouy. This synthesis was made by Stern in 1924 in his adsorption theory of the double layer. According to the Stern picture, part of the ions in solution stick to the electrode, forming the Helmholtz sheet of the double layer with a thickness corresponding to the average radius of the electrolyte ions [2]. The remaining ions in the double layer are diffusely spread out with decreasing charge density. Like Gouy, Stern neglected the size of the ions in the diffuse portion of the double layer. Besides, Stern suggested that in the Helmholtz region the ions are held not

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[1] A certain agreement is observed near the electrocapillary maximum, where the double layer must have the most diffuse structure owing to the small charge on the metal.

[2] Here Stern followed the path outlined by Debye and Hückel in their second approximation. Thus, the advances in the theory of solutions contributed in their turn to the development of the theory of the double layer at the electrode-electrolyte interface.

only by electrostatic forces but also by forces of specific adsorption, which are of noncoulombic origin. In solutions containing capillary-active ions, the number of such ions in the Helmholtz double layer may therefore not be equivalent to the charge on the metal surface but exceed it by a certain amount depending on the properties of

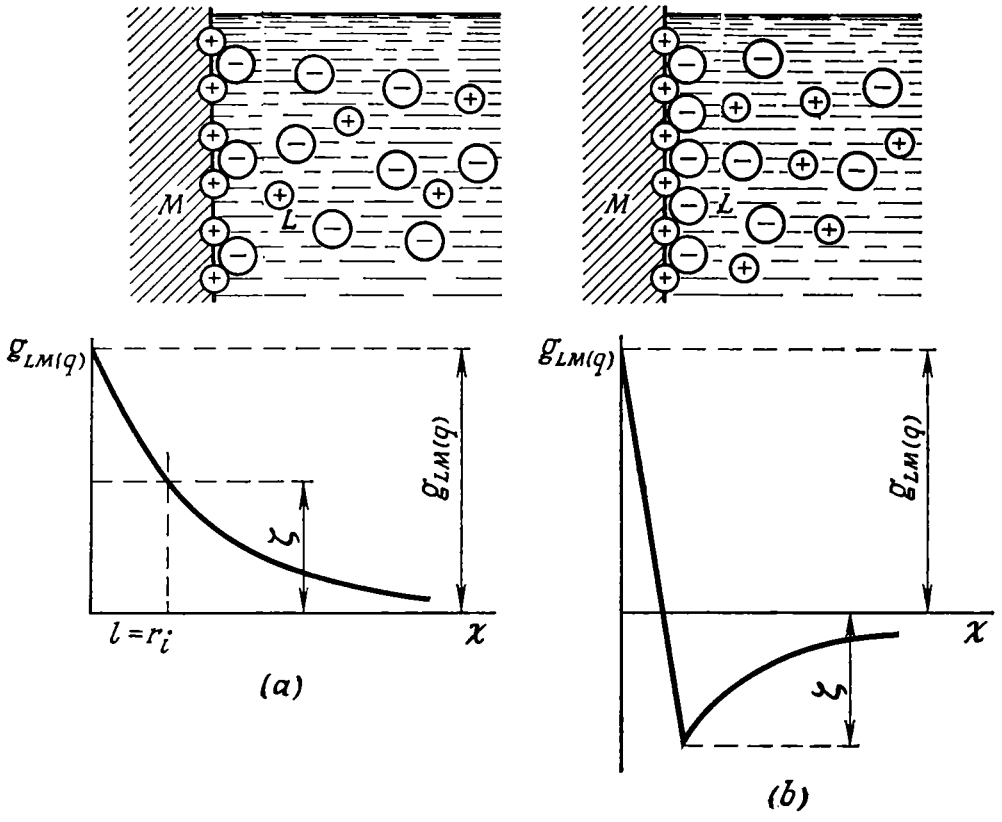

Fig. 11.4. The Stern model of the double layer. The molecular picture (top) and variation of potential with distance (bottom) for solutions of capillary-inactive substances (*a*) and solutions containing capillary-active anions (*b*)

the ions and the charge of the metal. Thus, according to Stern, two models of the double layer should be distinguished, one pertaining to solutions of capillary-inactive electrolytes and the other to solutions containing specifically adsorbed ions (Fig. 11.4). As before,

$$q_M = -q_L$$

However, in contrast to the Helmholtz and Gouy-Chapman models the Stern model pictures the charge density q_L on the solution side as consisting of two parts—the charge density in the Helmholtz layer q_H and the charge density in the diffuse layer q_d:

$$q_L = q_H + q_d = -q_M \qquad (11.7)$$

The quantity q_L can be determined by the formula

$$q_L = \frac{D}{4\pi r_i}(g_{LM(q)} - \zeta) \tag{11.8}$$

which differs from Eq. (11.3) of the parallel-plate model in that it contains a potential fall in the Helmholtz region of the double layer instead of the potential difference $g_{LM(q)}$.

Taking into account that beyond the distance r_i the charges in the double layer are distributed diffusely, one can write the following equation for q_d:

$$q_d = \sqrt{\frac{DRTc}{2\pi}}\left(e^{\frac{F\zeta}{2RT}} - e^{-\frac{F\zeta}{2RT}}\right) \tag{11.9}$$

As distinct from the Gouy theory, the quantity q_d in Eq. (11.9) depends not on the whole metal-solution potential difference but on that part of it which covers the potential drop in the diffuse portion of the double layer. In order to find the value of q_H, Stern assumes that the energy of the ion on the metal surface and in the solution is not the same. It differs by a value made up of the electrical work of transferring the ion from the bulk of the solution into the Helmholtz layer, $\pm F\zeta$, and the energy of ion adsorption Φ. Using the same argument as in the familiar derivation of the Langmuir adsorption isotherm, Stern arrives at the following equation:

$$q_H = F\Gamma_{max}\left(\frac{1}{1+\frac{1}{c}e^{\frac{\Phi_- - F\zeta}{RT}}} - \frac{1}{1+\frac{1}{c}e^{\frac{\Phi_+ + F\zeta}{RT}}}\right) \tag{11.10}$$

where Γ_{max} = maximum number of ions capable of being adsorbed on a unit surface area

Φ_- and Φ_+ = energies of adsorption of electrolyte anions and cations.

Combining Eqs. (11.8), (11.9) and (11.10), Stern obtains the general equation (known as the *Stern equation*) for uni-univalent electrolytes:

$$\underbrace{\frac{D}{4\pi r_i}(g_{LM(q)} - \zeta)}_{q_L} = \underbrace{F\Gamma_{max}\left(\frac{1}{1+\frac{1}{c}e^{\frac{\Phi_- - F\zeta}{RT}}} - \frac{1}{1+\frac{1}{c}e^{\frac{\Phi_+ + F\zeta}{RT}}}\right)}_{q_H} + \underbrace{\sqrt{\frac{DRTc}{2\pi}}\left(e^{\frac{F\zeta}{2RT}} - e^{-\frac{F\zeta}{2RT}}\right)}_{q_d} \tag{11.11}$$

The Stern theory allows one to define the zeta potential as the potential fall beyond the Helmholtz double layer, i.e., as the potential fall in the diffuse portion, where the ions are no longer strongly bound with the metal surface [1]. Thus defined, the ζ potential should not coincide with $g_{\mathrm{ML}(q)}$ or with the Nernst potential, and this is confirmed by experiment. From the model presented in Fig. 11.4 it follows that in solutions of capillary-active electrolytes the ζ potential not only does not coincide with the total potential difference in magnitude but may also be opposite in sign. Thus, Stern's theory was able, unlike the Helmholtz and Gouy-Chapman theories, to account for the experimentally observed recharging of the surface of a solid body and the change of sign of the electrokinetic potential.

Equation (11.11) shows that as $c \to 0$ its right-hand side must also tend to zero and, consequently,

$$g_{\mathrm{LM}(q)_{c\to 0}} \to \zeta$$

i.e., at an infinitely small concentration all the charges in the solution are randomly distributed and the double-layer structure is described by the Gouy-Chapman theory. Conversely, as the concentration increases the degree of diffusion will diminish since q_{H} increases proportionally to the concentration c to the first power, while q_d increases proportionally to $c^{1/2}$, i.e., slower than q_{H} and, consequently, for concentrated solutions the quantities q_d and ζ may be disregarded as compared with q_{H} and $q_{\mathrm{LM}(q)}$. In concentrated solutions the structure of the double layer is closely similar to the model proposed by Helmholtz. In the region of moderate concentrations where ζ is comparable with RT/F in magnitude, its dependence on concentration can be expressed by the following approximate equations based on the Stern formula:

(1) for positive values of ζ

$$\zeta = B - \frac{RT}{F} \ln c \tag{11.12}$$

(2) for negative values of ζ

$$\zeta = B' + \frac{RT}{F} \ln c \tag{11.13}$$

where B and B' may be taken as approximately constant quantities for conditions under which the charge on the metal surface does not change sign.

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[1] Equation (11.11) corresponds to the assumption that only the first ion layer adjacent to the metal surface is stationary; if the bonding between the ions and the electrode remains sufficiently strong in one or several subsequent ionic layers, the value of the zeta potential contained in the equations of the Stern theory must be larger than the ζ potential determined experimentally from the results of electrokinetic measurements.

The Stern theory yields a correct interpretation of the dependence of the shape of the electrocapillary curve on the concentration and nature of the electrolytes present, though, as pointed out by Esin and Markov on experimental evidence (the Esin-Markov effect) it does not provide quantitative agreement with experiment. In calculating the capacity by the Stern formula it is necessary to remember, in accordance with the Stern model, that the total capacity C of the double layer is composed of the capacity C_H of the Helmholtz region and the capacity C_d of the Gouy region of the double layer, the latter being in series with C_H:

$$\frac{1}{C}=\frac{1}{C_H}+\frac{1}{C_d} \qquad (11.14)$$

With the assumptions made by Stern the capacity of the diffuse layer (the Gouy region) must be considerably greater than that of the Helmholtz region and, as follows from Eq. (11.14), the total capacity is determined mainly by the capacity of the Helmholtz portion of the double layer. The determination of the capacity by the Stern theory therefore leads to results consistent with experiment both in the magnitude of the capacity and in the character of its dependence on the electrode potential and the solution concentration.

11.4. FURTHER DEVELOPMENT OF THE DOUBLE-LAYER THEORY

The Stern theory is a more or less correct reflection of the structure and properties of the electrical double layer. Both the theory and the corresponding double-layer model are used in investigations of electrochemical phenomena in which the double-layer structure plays an important role. The Stern theory, however, as admitted by its author, is not free of defects.

Many attempts have been made to elaborate such a theory of the double layer that would agree quantitatively with experimental data. For example, Reuss (1926-28) suggested that inside the metal, too, the charges are not all localized in one plane, but are distributed in the bulk of the metal with gradually decreasing density. The concept of two diffuse layers on either side of the interface is hardly applicable to the case where one of the contiguous phases is a metal. It may hold true for the boundary between ion-conducting phases and also for the interface between a semiconductor and a solution. Esin and Shikhov (1943) improved the Stern theory by taking into account discreteness-of-charge effects. They assumed that adions (specifically adsorbed ions) will be present in the double layer as mutually associated ion pairs, each pair consisting of an anion and a cation. This idea was further elaborated by Ershler (1946), who

advanced the viewpoint that the hexagonal array of the adions associated with a distorted ionic atmosphere on the solution side of the interface is the most probable. The Ershler model permits a satisfactory interpretation of the role of capillary-active ions in the shift of the electrocapillary maximum.

The theory of the double-layer structure was further developed in the works of Frumkin and his school and also of Grahame, Parsons, Devanathan and other workers. According to these authors two planes should be distinguished in the dense portion of the double layer: the inner and outer Helmholtz planes. The inner Helmholtz plane (referred to as IHP) is composed of specifically adsorbed ions, partly or completely dehydrated and forming dipoles with the metal. The outer Helmholtz plane (OHP) contains hydrated ions drawn to the metal surface by electrostatic forces. Between the OHP and the bulk of the solution is a diffuse layer. It has been shown that in many cases this model of the double layer has a number of advantages over the Stern picture. It provides a more comprehensive interpretation of experimental regularities. Much attention is focussed at present on the role of solvent molecules and adsorbed uncharged particles in the formation of a double layer at the metal-solution interface.

PART FIVE

Nonequilibrium (Irreversible) Electrode Processes

The practical utilization of electrochemical systems (as chemical sources of current or as electrolytic cells) is always associated with an electrochemical reaction proceeding in one direction at a finite rate. Natural electrochemical processes such as the corrosion of metals under the influence of the environment, also proceed in one direction at a perceptible rate. In both cases, therefore, electrochemical systems are not at equilibrium and their properties are essentially different from the properties of the corresponding equilibrium (reversible) systems.

Since the overall reaction in an electrochemical system, or cell, is composed of electrode reactions, the behaviour of each of the electrodes under irreversible conditions must differ from their behaviour under equilibrium conditions. The equilibrium state of an electrode can be characterized as follows.

1. The rate at which an electrochemical reaction proceeds in the anodic and cathodic direction is the same on the equilibrium electrode as a whole and on any portion of it sufficiently large as compared with the size of molecules. If the electrode reaction can be represented as

$$M^{z+} + ze = M$$

the transfer of one and the same type of ions M^{z+} across the electrode-electrolyte interface occurs at equal frequency in both directions. Since any electrochemical reaction involves charged particles, the frequency of the transfer of charged particles in either direction must be equivalent to a certain amount of current. At equilibrium

$$I_a = I_c = I^0$$

where I_a and I_c = currents corresponding to anodic and cathodic processes

I^0 = exchange current density equal to I_a and I_c each in absolute value; it characterizes the kinetics of ion exchange under equilibrium conditions.

2. The rates of one and the same electrode reaction in two opposite directions being equal, no changes occur in the qualitative and quantitative composition of a system at equilibrium. The nature and mass of electrode as well as the composition of the electrolyte remain unaltered.

3. Since the partial currents I_a and I_c are equal, it follows that under the conditions of established equilibrium the charge on the metal with respect to the solution and hence the electrode potential are independent of time; they are determined only by the composition of the system, its temperature and pressure. The electrode potential ε under these conditions is called the *reversible* or *equilibrium electrode potential.* Its value (on the arbitrary scale) can be calculated with the aid of general thermodynamic equations provided the electrode reaction, the activities of the reacting substances, the temperature and pressure are known.

4. The emf of an equilibrium electrochemical system is determined by the free-energy change in the reaction taking place in the cell.

A nonequilibrium electrochemical system, i.e., a system in which electrochemical reactions proceed in a given direction at a finite rate, is characterized by the following features.

1. The rate of an electrochemical reaction in the anodic and cathodic directions is not the same

$$I_a \neq I_c \neq I^0$$

Neither of the partial currents is equal to the exchange current density. As a rule, in a nonequilibrium (irreversible) electrochemical system one of the two possible electrode reactions (corresponding to the two electrodes of the cell) proceeds predominantly in the anodic direction and for this reaction

$$I_a > I_c$$

and the other, predominantly in the cathodic direction and for it

$$I_a < I_c$$

In the case of the reaction

$$M^{z+} + ze = M$$

the transfer of one and the same type of ions across the electrode-electrolyte interface takes place at different frequencies.

2. Because the reaction proceeds predominantly in one direction the mass (and often also the nature) of the electrode and the compo-

sition of the solution near the electrode are ultimately found to be changed as compared with the state of equilibrium.

3. The electrode potential ε_I is not, in a general case, equal to the equilibrium electrode potential ε_r and cannot be calculated thermodynamically. Its value depends not only on the nature of the system, the temperature and pressure, but also on the current intensity.

4. When a steady-state process is set up, the nonequilibrium electrode potential may be found practically independent of time, like the equilibrium potential. This steady-state value of the electrode potential under the applied current is called the *stationary* or *steady-state potential* ε_s.

5. The magnitude of the voltage E_i for irreversible electrochemical systems is different from the reversible value of emf E_r. The voltage of galvanic cells is in this case lower and the voltage across the electrolytic cell larger than the reversible emf. The value of E_i is not determined unambiguously by the change in the free energy of the corresponding reaction.

Thus, for an irreversible electrochemical system, or cell, there must exist a definite relationship between the current intensity and the rate of the chemical change taking place in it and also between the current intensity and the voltage E_i or the potentials involved in the electrode system.

CHAPTER 12

The Chemical Effect of Electric Current

12.1. FARADAY'S LAWS

12.1.1. THE ESSENCE OF FARADAY'S LAWS. ELECTROCHEMICAL EQUIVALENTS

Since the passage of an electric current through electrochemical systems, or cells, entails chemical reactions, a definite relationship must exist between the quantity of electricity passed through the cell and the amount of chemically reacted matter. This relationship was discovered by Michael Faraday and expressed in the first quantitative laws of electrochemistry later named *Faraday's Laws of Electrolysis.*

Faraday's first law states that the amount of reacted substance is directly proportional to the quantity of electricity passed through the cell. This law is mathematically expressed by the equation

$$\Delta m = k_e It = k_e q \tag{12.1}$$

where Δm = amount of chemically reacted substance
k_e = proportionality factor
q = quantity of electricity equal to the product of the current I by the elapsed time t.

If $q = It = 1$, then $\Delta m = k_e$, i.e., the coefficient k_e represents the amount of chemical change produced by a unit quantity of electricity. The coefficient k_e is called the *electrochemical equivalent.* As the unit quantity of electricity may be expressed in various ways (1 C = 1 A-sec; 1 F = 26.8 A-hr = 96.500 C), a distinction should be made, for each particular reaction, between electrochemical equivalents corresponding to these three units: ${}_{\text{A-sec}}k_e$, ${}_{\text{A-hr}}k_e$ and ${}_{\text{F}}k_e$. For gaseous and liquid substances the expression for the electrochemical equivalent may contain volume instead of mass. Electrochemical equivalents for some important reactions are listed in Table 12.1.

Faraday's second law reflects the relation between the amount of chemically reacted matter and its nature. From the second law it follows that at a constant current the masses of the reacted substances are interrelated in the same way as their chemical equivalents A:

$$\frac{\Delta m_1}{A_1} = \frac{\Delta m_2}{A_2} = \frac{\Delta m_3}{A_3} = \ldots = \text{const} \tag{12.2}$$

If the faraday is chosen as the unit quantity of electricity, then

$$\Delta m_1 = {}_{\text{F}}k_{e1} = A_1, \quad \Delta m_2 = {}_{\text{F}}k_{e2} = A_2 \quad \text{and} \quad \Delta m_3 = {}_{\text{F}}k_{e3} = A_3$$

TABLE 12.1

Electrochemical Equivalents *

Element	Atomic weight	Reaction	Change of valency	A-sec k_e, g/A-sec×10³
Ag	107.88	$Ag^+ + e = Ag$	1	1.1179
Al	26.97	$Al^{3+} + 3e = Al$	3	0.0932
Be	9.01	$Be^{2+} + 2e = Be$	2	0.0461
Br	79.92	$^1/_2Br_2 + e = Br^-$	1	0.8282
Br	79.92	$BrO_4^- + 8H^+ + 7e = {}^1/_2Br_2 + 4H_2O$	7	0.11831
Cd	112.41	$Cd^{2+} + 2e = Cd$	2	0.5824
Cl	35.46	$^1/_2Cl_2 + e = Cl^-$	1	0.3674
Cl	35.46	$ClO_3^- + 6H^+ + 5e = {}^1/_2Cl_2 + 3H_2O$	5	0.0735
Cl	35.46	$ClO_4^- + 8H^+ + 7e = {}^1/_2Cl_2 + 4H_2O$	7	0.05249
Cr	52.01	$Cr^{3+} + 3e = Cr$	3	0.1796
Cr	52.01	$Cr^{2+} + 2e = Cr$	2	0.2695
Cr	52.01	$CrO_4^{2-} + 8H^+ + 6e = Cr + 4H_2O$	6	0.0898
Cu	63.57	$Cu^+ + e = Cu$	1	0.6588
Cu	63.57	$Cu^{2+} + e = Cu^+$	1	0.6588
Cu	63.57	$Cu^{2+} + 2e = Cu$	2	0.3294
Fe	55.84	$Fe^{3+} + e = Fe^{2+}$	1	0.5786
Fe	55.84	$Fe^{2+} + 2e = Fe$	2	0.2893
Fe	55.84	$Fe^{3+} + 3e = Fe$	3	0.1929
H	1.008	$H^+ + e = {}^1/_2H_2$	1	0.0104
Hg	200.61	$Hg^+ + e = Hg$	1	2.0789
Hg	200.61	$Hg^{2+} + 2e = Hg$	2	1.0394
I	126.92	$^1/_2I_2 + e = I^-$	1	0.1879
K	39.10	$K^+ + e = K$	1	0.4051
Mg	24.32	$Mg^{2+} + 2e = Mg$	2	0.1260
Mn	54.93	$Mn^{2+} + 2e = Mn$	2	0.2846
Mn	54.93	$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	2	0.2846
Na	22.30	$Na^+ + e = Na$	1	0.2383
Ni	58.69	$Ni^{3+} + e = Ni^{2+}$	1	0.6082
Ni	58.69	$Ni^{2+} + 2e = Ni$	2	0.3041
O	16.00	$^1/_2O_2 + 2H^+ + 2e = H_2O$	2	0.0829
Pb	207.21	$Pb^{2+} + 2e = Pb$	2	1.0736
Pb	207.21	$Pb^{4+} + 2e = Pb^{2+}$	2	1.0736
Pt	195.23	$Pt^{2+} + 2e = Pt$	2	1.0116
Pt	195.23	$Pt^{4+} + 4e = Pt$	4	0.5058
Sn	118.70	$Sn^{2+} + 2e = Sn$	2	0.6150
Sn	118.70	$Sn^{4+} + 2e = Sn^{2+}$	2	0.6150
Sn	118.70	$Sn^{4+} + 4e = Sn$	4	0.3075
Ti	47.90	$Ti^{2+} + 2e = Ti$	2	0.2477
Zn	65.88	$Zn^{2+} + 2e = Zn$	2	0.3388

* The values of electrochemical equivalents have been obtained by dividing the atomic weights of elements by the product of the valency change in the course of the reaction and 96,500 C. The data given can be used to calculate electrochemical equivalents expressed in other units. Knowing the molecular weight of the substance participating in the reaction, one can convert the tabulated data to the electrochemical equivalents of compounds containing the given element.

from which, in accordance with the definition of ${}_{\mathrm{F}}k_e$ at $q = 1$ F,

$$\frac{\Delta m_1}{A_1} = \frac{\Delta m_2}{A_2} = \frac{\Delta m_3}{A_3} = \ldots = \text{const} = 1 \qquad (12.3)$$

The last equation makes it possible to combine the two Faraday laws into a single general law, by which the amount of electricity equal to one faraday (or 96,500 coulombs or 26.8 amperes per hour) invariably produces an electrochemical change of one gram-equivalent of a substance.

12.1.2. CURRENT EFFICIENCY

Faraday's laws are the most general and exact quantitative laws of electrochemistry. In most cases, however, the amount of a given substance undergoing electrochemical change is smaller than could be expected on the basis of Faraday's laws. For example, if a current is passed through an acidified solution of zinc sulphate, about 0.6 g-eq of zinc instead of 1 g-eq is usually deposited per one faraday of electricity consumed. Similarly, if chloride solutions are subjected to electrolysis, the passage of one faraday of electricity will produce not one but a little less than 0.9 g-eq of gaseous chlorine. These examples however are only apparent deviations from Faraday's laws. These laws postulate that the amount of a substance (simple or complex) undergoing chemical change as a result of the passage of one faraday of electricity corresponds to one gram-equivalent. In the first example given above two reactions take place at the cathode:

(a) the electrodeposition of zinc

$$Zn^{2+} + 2e = Zn$$

(b) the formation of hydrogen gas

$$2H^+ + 2e = H_2$$

If one determines not only the amount of deposited zinc, but also the quantity of evolved hydrogen gas, the total amount of product formed will be 1 g-eq (0.6 g-eq of zinc and 0.4 g-eq of hydrogen). Similarly, the results obtained with the evolution of chlorine will not contradict Faraday's laws, considering that a certain fraction of current is consumed for the formation of oxygen and that the chlorine liberated at the anode may partly pass into solution again as a result of secondary chemical reactions, for example, according to the equation

$$Cl_2 + H_2O = HCl + HClO$$

To take into account the effect of parallel and secondary reactions, the concept of *current efficiency*, or *current yield*, B_c, has been intro-

duced. Current efficiency is the fraction of current passing through a cell, which accomplishes the desired electrode reaction:

$$B_c = \frac{q_i}{\Sigma q_i} \tag{12.4}$$

or, expressed as a percentage,

$$B_c = \frac{q_i}{\Sigma q_i} 100 \text{ per cent} \tag{12.5}$$

where q_i = quantity of electricity consumed for a given reaction
Σq_i = total amount of electricity passed.

Thus, in the first example the current yield of zinc is 60 per cent and that of hydrogen, 40 per cent. The expression for current efficiency is often written down in the form

$$B_c = \frac{q_c}{q_a} 100 \text{ per cent} \tag{12.6}$$

where q_c = quantity of electricity calculated by Faraday's formula
q_a = quantity of electricity that has actually been consumed to change a given amount of substance.

Current efficiency may also be defined as the ratio of the amount of the converted substance, Δm_a, to the amount of the substance that would react if the whole amount of current were used to accomplish the given reaction, Δm_c:

$$B_c = \frac{\Delta m_a}{\Delta m_c} 100 \text{ per cent} \tag{12.7}$$

If among several possible electrode processes only one is desirable, then its current efficiency should be made as high as possible. There are systems in which the whole current is expended on a single electrochemical reaction. Such electrochemical systems, or cells, are used to measure the quantity of electricity passed and are called *coulometers*. There are three principal types of coulometer: the weight, volume and titration coulometers. In *weight coulometers* (silver and copper coulometers), the quantity of electricity passed is calculated from the increase in the weight of the cathode. In *volume coulometers*, the total volume of substances formed (gas in the hydrogen coulometer and liquid mercury in the mercury coulometer) is measured. In *titration coulometers*, the quantity of electricity passed is determined from data on the titration of substances generated in solution by the electrode reaction. In this method anodic dissolution of silver (the Kistyakovsky coulometer) or electrolytic oxidation of iodide ions is usually used.

12.1.3. POSSIBLE DEVIATIONS FROM FARADAY'S LAWS

Apart from systems for which Faraday's laws are quantitatively justified, there are also systems in which deviations from these laws are possible. For example, calculations based on Faraday's laws will prove erroneous in the case of an electrolytic cell consisting

of two platinum electrodes immersed in a solution of metallic potassium in liquid ammonia. Being a conductor of mixed conductance, this solution exhibits noticeable metallic conduction and during electrolysis a considerable part of electrons are capable of leaving the electrode and passing directly into solution without causing any chemical change. Similar phenomena are observed when a current is passed through gases. Such systems however are not true electrochemical cells consisting only of first- and second-class conductors. In true electrochemical cells, the transfer of electrons from the electrode into the solution and vice versa is invariably associated with a chemical change and so it obeys Faraday's laws. Being a natural and inevitable consequence of the very nature of electrochemical transformation, Faraday's laws should at the same time be regarded as the most reliable criterion of a true electrochemical system.

12.1.4. FARADAY'S LAWS AND THE RATE OF ELECTROCHEMICAL PROCESSES

The rate of an electrochemical reaction v is defined, like that of an ordinary chemical reaction, as the amount of substance converted in unit time, i.e.,

$$v = \pm \frac{d\Delta m}{dt} \tag{12.8}$$

Since the amount of chemical change produced by electrolysis is directly proportional to the total amount of electricity passed, one can write, using Eq. (12.1),

$$v = \pm \frac{d\Delta m}{dt} = k_e \frac{dq}{dt} = k_e I \tag{12.9}$$

and so the rate of an electrochemical reaction is found to be proportional to the current I. As k_e is constant for each particular reaction, the current I can then be conveniently used to express the rate of any electrochemical change. If the current is referred to one faraday, the quotient I/F will be the rate of an electrochemical reaction in terms of gram-equivalents of substance and the quotient I/zF the reaction rate in terms of gram-molecules (gram-ions) of the substance.

A specific feature of electrochemical reactions is that they all occur at the electrode-electrolyte interface and therefore the rate of these reactions depends on the surface area Ω of the interface. The rate of an electrochemical reaction is thus usually referred to the unit surface area of the interface and expressed in terms of current density i:

$$i = \frac{I}{\Omega} \tag{12.10}$$

The rate of electrochemical reactions is most often measured in A/cm^2 or (in industrial electrochemistry) in A/m^2.

Using Faraday's laws, one can calculate the quantity of electricity needed to produce the required yield of electrolytic product. Thus, at a current efficiency of 100 per cent one and the same amount of electricity equal to one faraday is required to produce one gram-equivalent of any substance. Faraday's laws determine the consumption of the quantity of electricity and not of electrical energy, which will not be the same in producing one and the same number of gram-equivalents of a substance; the consumption of electrical energy depends on the nature of the substance, the type of the reaction producing this substance and also on the reaction conditions. If the value of F yields the quantity of electricity required to produce one gram-equivalent of a substance, the electrical energy consumed will in this case be equal to the product FE. For each substance there is a specific value of voltage E across the cell, which may vary depending on the conditions under which the electrochemical reaction is conducted.

The Swedish chemist Berzelius, a contemporary of Faraday, doubted the validity of Faraday's laws alleging that they were in contradiction to thermochemical data, according to which the energy effects associated with different reactions are not equal. In his criticism Berzelius missed out the difference between the quantity of electricity and the amount of electrical energy.

In industrial electrochemistry, apart from the quantity of electricity, the electrical power consumed for carrying out a particular technological electrochemical process is of crucial importance.

12.2. ELECTROANALYSIS AND COULOMETRY

The transformation of substances on electrodes under the influence of electric current obeys Faraday's laws. This relationship forms the basis of two quantitative electrochemical methods of investigation and analysis called *electroanalysis* and *coulometry*.

12.2.1. ELECTROANALYSIS

Electroanalysis, or electrogravimetry, is based on measuring the weight of the deposit formed on the electrode surface as a result of the passage of a quantity of electricity sufficient for a complete, or practically complete, deposition of the substance. Electrodeposition may occur on the cathode (discharge of metallic ions with the deposition of a metal) or on the anode (discharge of anions with the formation of the corresponding salts or oxides). Knowing the chemical composition of the deposit, one can easily calculate from the weight of the deposit the amount of a sought-for constituent in the original solution. Since the quantity of electricity consumed for the deposition of the substance is not included in subsequent calculations, the current efficiency in electroanalysis may not

necessarily be equal to 100 per cent. A fraction of the current may be consumed for other electrode reactions provided the latter do not change the composition of the deposited metal or loosen it mechanically, or reduce its adhesion to the electrode. In this connection, the wastage of a certain amount of current on the evolution of hydrogen or oxygen can be tolerated. It should however be kept in mind that the lower the current yield of the substance to be determined, the more time will be required for electrolysis.

The electroanalysis of solutions containing only one sought-for ionic species is carried out at a constant current. As this component is deposited and the solution is depleted the electrode potential gradually changes. At a predetermined current the potential of the cathode assumes more negative, and that of the anode more positive values. This shift of the potential can be estimated, to a first approximation, from the Nernst formula:

$$\varepsilon = \varepsilon^0 \pm \frac{b^0}{z} \log c$$

where c is the concentration of the unknown ions and the plus and minus signs refer, respectively, to cations and anions. If in the course of electroanalysis the potential departs from its original value, say, by an amount of $3b^0/z$, i.e., is about 0.18 V for univalent (3×0.06) and 0.09 V for bivalent (3×0.03) ions, the ratio of the initial concentration of the ions to be determined to their concentration at this moment will be equal to 10^3. The extent of deposition will in this case be close to 99.9 per cent, and the determination error, of the order of 0.1 per cent. Thus, by observing the change of the potential, the completion of the deposition process can be recognized. In practice, the end-point of the electrolysis is identified with the aid of a suitable visual indicator or by special electrochemical methods.

Electrogravimetry at constant current is not recommended for analysis of solutions containing different ionic species since the changing electrode potential may coincide with the deposition potential of ions other than those to be determined with subsequent codepositon of the former. As a result, the composition of the deposit will become indeterminate. In such cases more reliable results are provided by another method in which not the current but the electrode potential is kept constant[1]. In this method, a value of potential is chosen which provides deposition of only one ionic species. This can be done if the composition of the solution being analysed and the electrochemical characteristics of the ions present are known. For example, if the solution contains cupric ions Cu^{2+} and cadmium ions Cd^{2+}, whose standard potentials are equal to +0.34 and −0.40 V,

[1] The first method can also yield reliable results if the ions present differ markedly in their electrode potential or when this difference is increased by binding simple ions into complex ions and by adjusting the pH of the solution.

respectively, then by maintaining the cathode potential between these two values (say, at about +0.20 V) deposition of cadmium can be completely prevented and the reaction made to proceed quantitatively to deposit metallic copper. Once all the copper is deposited, one can start determining the amount of cadmium by electrolysis at a less positive potential, for example, at —0.5 V; in the same way it is possible to determine a larger number of different ions present in the solution. The end-point of the electrolysis for each ionic species is identified by an abrupt decay of the current.

Electrical power needed to carry out electrogravimetry at constant current and at constant potential is supplied by an external constant-current source.

There is also a third electrogravimetric technique known as *internal electrolysis*[1]. In this method, an electrode pair consisting most often of a platinum cathode and an electronegative metal (e.g. zinc or magnesium) as the anode is immersed in the solution to be analysed. On completion of the external circuit through an ammeter and a controlling resistance, the anode begins to dissolve, passing into solution, and the required deposit forms on the platinum cathode; as a result the cell itself starts generating a current. To effect internal electrolysis, it is necessary that the electrode potential of the ions to be determined be more positive than that of the metal used as anode.

Internal electrolysis may be regarded as a modification of the electrogravimetric technique at a specified potential, whose value is controlled by the choice of anode. The end-point of the analysis in internal electrolysis is the decay of the current indicated by the ammeter.

Electrogravimetry is mainly used to determine the content of metallic ions capable of forming a compact, well-adhering deposit on the cathode. In many cases use is made of the possibility of producing corresponding deposits on the anode. For example, with certain conditions observed, lead can be quantitatively deposited on the anode as lead dioxide, and halides on a silver anode in the form of the corresponding silver salts.

In the electroanalysis of most metallic ions use is made of cylindrical gauze cathodes; platinum cathodes are usually employed, which are replaced with mercury cathodes when the content of the ions of alkali or alkali-earth metals is to be determined. Anodes are usually made of platinum in the form of wire spiral and placed inside cylindrical cathodes. To speed up electrolysis the solution is stirred vigorously, often by means of a rotating spiral anode. For the same purpose the analysis is conducted at an elevated temperature.

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[1] This method is also known as *spontaneous electrogravimetry* or *short-circuit electrolysis.—Tr.*

Electrogravimetric methods are widely used in laboratory work, especially in analysis of alloys. They are also employed for separation of different substances present in a solution and also as a concentration and beneficiation method. In the latter case electroanalysis is combined with other, more sensitive analytical methods (X-ray analysis, polarography, coulometry), replacing chemical methods of concentration associated with labour-consuming operations of precipitation, filtration and evaporation.

12.2.2. COULOMETRIC ANALYSIS

In coulometric analysis, the amount of a substance undergoing chemical change is calculated from the measured quantity of electricity (the number of coulombs, hence the name of this method). Coulometric analysis is based on Faraday's laws and its application is possible only if all the current passed is consumed for the desired electrode reaction, i.e., if a current efficiency of 100 per cent is maintained. With this condition observed one can find the amount of the sought-for constituent, m, by measuring the quantity of electricity passed, q:

$$m = k_e q \qquad (12.11)$$

In contrast to electrogravimetry, in coulometric analysis it is possible to determine substances not deposited on the electrode but remaining in the solution or vented into the surrounding atmosphere. Since even negligibly small amounts of current can be measured with an insignificant error, coulometry may be regarded as a highly sensitive and accurate method of analysis. Coulometry permits determination of substances present in amounts of 10^{-10} to 10^{-12} g-eq/litre, the error being about 1 per cent; when the amount of the substance being analysed is of the order of 10^{-3} to 10^{-5} g-eq/litre, the error is 0.1-0.3 per cent. For this reason, coulometric analysis is particularly valuable for producing ultrapure materials.

Like electrogravimetry, coulometric analysis is carried out either *at constant potential* or *at constant current*, depending on the solution composition and the possible number of electrode reactions involved. The constant-current procedure should be employed when the possibility of the occurrence of any reactions other than the main reaction on the electrode is excluded over a wide range of potentials. This is the most accurate and sensitive method of analysis. In constant-potential coulometry, the quantity of electricity passed is measured by means of a coulometer; in the constant-current method this is done by multiplying the current by the time of analysis.

The following examples illustrate the procedure of coulometric analysis. When the acidity of a solution is to be determined, platinum electrodes are used; the cathode is immersed directly in the solution to be analysed and the anode is separated from it by means of a porous diaphragm which provides chemical but not electrical isolation.

A constant current is passed through the solution under test until the solution becomes neutral, this being established with the aid of an indicator. The quantity of electricity consumed up to the neutralization point is then converted to the number of gram-equivalents of hydrogen. Knowing the volume of the original solution, one can calculate its acidity.

To determine cadmium present in a solution together with thallium, a mercury cathode and a platinum anode are used. The potential of the mercury cathode must ensure the discharge of only cadmium ions. The end-point of cadmium deposition is identified by the fall of the current to a constant value. The amount of electricity passed is found by means of a coulometer in series with the electrolytic cell and then the amount of cadmium in the solution is calculated using its known electrochemical equivalent. If the amount of thallium in the same solution is also to be determined, the analysis is conducted in the same way as for cadmium, with the only difference that the potential of the mercury cathode is shifted to the required value.

The amount of anions (in particular halide ions) in the solution can also be found coulometrically. In this case the deposition is effected at the anode, using either metals reacting quantitatively with anions to form sparingly soluble compounds, or platinum, on which the oxidation of a number of anions can be carried out with a current efficiency of 100 per cent.

The above examples illustrate *direct*, or *primary*, *coulometry*. Another method, which has recently been considerably developed, is *indirect*, or *secondary*, *coulometry*, in which the titration reagent is generated directly within the solution (this method is therefore also called *coulometric titration with an electrolytically generated reagent* or *internal-generation method*). In this case one measures the number of coulombs used for oxidation or reduction of a chemical substance, which is added in excess to the solution prior to the experiment and is capable of reacting quantitatively with the sought-for constituent.

Many reactions employed for conventional volumetric analysis can be used for this purpose. Suppose, for example, that we are to determine the amount of thiosulphate. Direct coulometric determination by anodic oxidation does not ensure sufficient accuracy since this reaction proceeds at a current efficiency lower than 100 per cent and is accompanied by oxygen evolution. Thiosulphate can be titrated with an iodine solution by addition of a starch indicator or potentiometrically according to the reaction

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

The same reaction can be carried out coulometrically if an excess solution of potassium iodide is added to the thiosulphate solution

and a current is passed between platinum electrodes immersed in the test solution. The iodide is oxidized at the anode to elementary iodine:

$$2I^- = I_2 + 2e$$

which reacts quantitatively with the thiosulphate. Having determined the number of coulombs used for the complete oxidation of thiosulphate by iodine, one can calculate the amount of thiosulphate present by using Eq. (12.11). Suppose 10 coulombs of electricity has been used for the titration of the sample. The electrochemical equivalent of thiosulphate in the reaction under consideration is

$$\frac{M_{S_2O_3^{2-}}}{zF} = \frac{112.13}{96,500} = 1.16 \times 10^{-3} \text{ g/C}$$

The amount of thiosulphate in the sample being analysed must then be

$$m = 1.16 \times 10^{-3} \times 10 = 1.16 \times 10^{-2} \text{ g}$$

The same principle may be used to carry out cerimetric titration of iron (in which anodically-generated ions of tetravalent cerium, Ce^{4+}, oxidize ferrous ions to ferric), determination of permanganate (by reducing it with cathodically generated ferrous ions) and many other indirect coulometric analyses. Coulometric titration is instrumentally more complicated than indicator or even potentiometric titration. For this reason coulometry finds only limited practical use in ordinary chemical analysis. It is advantageous, however, when determining microquantities of dissolved substances or carrying out automatic titrations. The preparation and use of very dilute titrant solutions required for volumetric determination of small quantities of dissolved substances involves considerable errors and inconveniences. Coulometric titrations do not require the use of such solutions because the substance to be determined is either transformed directly on the electrode or titrated with a reagent generated electrolytically on one of the electrodes within the test sample. In either case the determination is based on the quantity of electricity consumed; even very small amounts of current can be measured with a high degree of accuracy.

Since all the reactions used in coulometry involve electrons, the latter may be regarded as a sort of universal reagent specific for this method.

Coulometry is especially convenient where titration must be fully automated since there arise no difficulties usually associated with automatic control of the delivery of the titrating solution. Coulometry also finds use in carrying out various electrochemical investigations. In particular, it is employed for determining the thickness of metallic coatings, the amounts of oxides or salts formed on electrodes, the extent of coverage of metal surfaces with adsorbed hydrogen or oxygen, etc.

CHAPTER 13

The Kinetics of Electrode Processes

13.1. BASIC CONCEPTS

13.1.1. THE ELECTROMOTIVE FORCE OF POLARIZATION

The passage of an electric current through an electrochemical system, or cell, is associated not only with corresponding chemical reactions but also with the change of its electrical characteristics, primarily the electromotive force and electrode potentials, as compared with their initial values in the absence of current. If the electrochemical system is an electrolyser[1] (electrolytic cell), the voltage across it at a given current intensity will be higher than the reversible emf of the same system

$$E_{I(ec)} > E_r$$

Conversely, if an electrochemical system generates a current, i.e., is a chemical source of current[2]—a galvanic cell or accumulator, then

$$E_{I(gc)} < E_r$$

The thermodynamics of electrochemical systems is incapable of elucidating the causes of the change of the emf upon transition to the irreversible state and ascertaining the relation between this change and the rate of an electrochemical reaction, i.e., the magnitude of the current (or current density) passed through the system. Resort has therefore to be made to certain assumptions of nonthermodynamic nature.

The first assumption concerning the cause of this phenomenon is that the difference between the reversible emf and the voltage arises from ohmic losses of voltage. In this case the voltage required to carry out a reaction in an electrolytic cell is composed of the reversible emf E_r (determined by the free-energy change) and the potential fall in the electrolyte and at the electrodes E_{ohm} (which depends on the current density). This assumption explains the cause of an increase in the voltage across the cell during the passage of a current, as compared with the reversible emf of the same system. In a similar way, the decrease of the voltage across a galvanic cell when a current

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[1] An electrochemical substance producer (substance-producing device), also known as an *electrochemical reactor.—Tr.*

[2] An electrochemical energy producer (or energy-producing device). A *fuel cell* is also an example of such energy producer.—*Tr.*

is drawn from it may be attributed to the fact that part of the emf is consumed to overcome the resistance inside the cell. Ohmic losses of voltage are thus one of the factors responsible for the difference between the reversible emf and the actual operating potential. Experiment however shows that

$$E_{I(ec)} > E_r + E_{ohm} \tag{13.1}$$

and

$$E_{I(gc)} < E_r - E_{ohm} \tag{13.2}$$

Very often

$$|E_I - E_r| \gg E_{ohm} \tag{13.3}$$

The main cause for the change of the voltage across an electrochemical system when a current is driven into or withdrawn from it should therefore be sought not in ohmic losses but in the variation of electrode potentials with current intensity or density. When a current is imposed upon the cell, the potential of each of the two electrodes in the electrochemical system changes so that the voltage across the electrolytic cell increases and that across the galvanic cell reduces. The total change of electrode potentials on closed circuit is called the *emf of polarization* E_p. If, apart from the ohmic fall in voltage, the polarization emf is also taken into account, one can write the equations for the cell potential in both cases:

$$E_{I(ec)} = E_r + E_{ohm} + E_p \tag{13.4}$$

$$E_{I(gc)} = E_r - E_{ohm} - E_p \tag{13.5}$$

Equations (13.4) and (13.5) are concordant with experimental observations.

A rational implementation of an electrochemical process with a maximum electrical energy drawn from a chemical source of current (an energy producer) or a minimum amount of electricity consumed by an electrolyser (a substance producer) is possible only when the cause of the formation of the polarization emf is known and its nature well established. Since the polarization emf is a resultant quantity composed of the changes in the electrode potentials, it is necessary first of all to study the dependence of electrode potentials on current intensity. This task is handled by the kinetics of electrode processes.

13.1.2. ELECTRODE POLARIZATION

The difference between the operating electrode potential and the equilibrium potential is called the *electrode polarization*, or simply *polarization*, $\Delta\varepsilon$:

$$\Delta\varepsilon = \varepsilon_I - \varepsilon_r \tag{13.6}$$

The electrode potential ε_I and the polarization $\Delta\varepsilon$ are primarily functions of the current intensity; in the absence of current they are, respectively, equal to ε_r and zero.

The term electrode polarization is also used when with no external current imposed the electrode potential is not an equilibrium value but corresponds to the so-called *stationary*, or *steady-state*, *potential* ε_s (see below). The magnitude of the polarization is then determined by an equation analogous to Eq. (13.6), with the only difference that ε_s is substituted for ε_r:

$$\Delta\varepsilon = \varepsilon_I - \varepsilon_s \tag{13.7}$$

It is thought at present that the relationships between ε_I and I and between $\Delta\varepsilon$ and I are based on the kinetic laws characteristic of a particular electrode reaction. A study of the specific features of potential-current curves, which are also often called *polarization curves*, is therefore necessary for understanding the nature of electrode reactions. The tracing of polarization curves was for a long time practically the only method for investigating the kinetics of electrochemical processes; this method is still in use.

Any electrodic process is a complex heterogeneous reaction involving a number of consecutive steps. At some of these steps the reaction may take two or more parallel paths. To establish the number, nature and sequence of steps making up an electrode process is one of the main tasks of electrode kinetics. From chemical kinetics it is known that the rate of a multistep consecutive reaction is governed by the rate of the slowest of its steps, and that out of a number of parallel paths the most probable is the one that is least inhibited. The same principles apply to electrochemical processes. The occurrence of the electrode polarization is therefore directly associated with the step that determines the rate of the overall process, i.e., the slowest step. The elucidation of the nature of the slowest step (the rate-determining step, often abbreviated to rds) constitutes another principal task of electrochemical kinetics. On the other hand, the occurrence of a new path, which increases the reaction rate, may reduce the electrode potential, which may in some cases, for example, when the nature of the electrode process changes, become even lower than the reversible, or equilibrium, potential. This fall of the electrode potential and the process responsible for it is called *depolarization*.

The nature and the number of steps of each electrochemical process depend on the type of reaction involved. For example, in the electroreduction of trivalent ferric ions to divalent ferrous ions the first step of the process is the delivery of the ferric ions to the electrode surface (Fig. 13.1). When brought into contact with the electrode a trivalent ferric ion acquires an electron; this act of discharging gives birth to a bivalent ferrous ion and simultaneously results in the

rearrangement of the hydration sheath. The resulting ferrous ion must be removed from the electrode surface to leave a site for the next

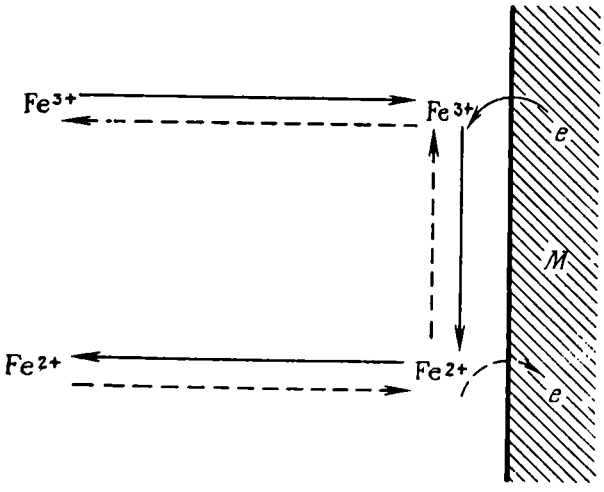

Fig. 13.1. Schematic representation of recharging of iron ions: $Fe^{3+} + e = Fe^{2+}$. The solid arrow indicates the forward process and the dashed arrow, the reverse process

ferric ions to be discharged. The oxidation of ferrous ions proceeds through the same steps but in reverse order.

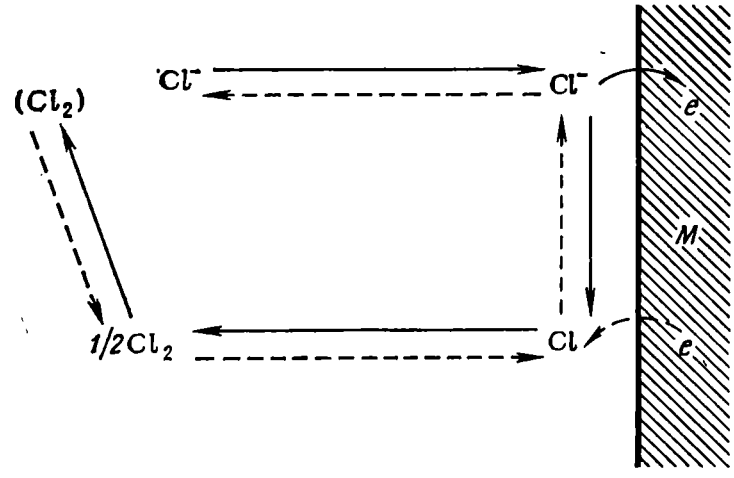

Fig. 13.2. Schematic representation of the electrode reaction of evolution and dissolution of chlorine: $Cl^- = {}^1/_2Cl_2$. The solid arrow indicates the forward process and the dashed arrow, the reverse process

The first step in the discharge of chloride ions also consists in the transport of these ions to the electrode-electrolyte interface (Fig. 13.2). Once a chloride ion enters the electric double layer it loses its electron, and is dehydrated and transformed into a chlorine

atom adsorbed on the electrode (the second step). At the third step the chlorine atoms formed are recombined into molecules [1]. The chlorine molecules move into the surrounding electrolyte and, having formed a saturated solution, escape into the atmosphere as gas bubbles (the final step). The dashed arrows in Fig. 13.2 indicate the steps of the reverse process of ionization of the chlorine gas.

The cathodic deposition of metallic silver from a solution of its simple salt (Fig. 13.3) starts off with the transport of silver ions to the electrode surface. Having entered the double layer, the silver

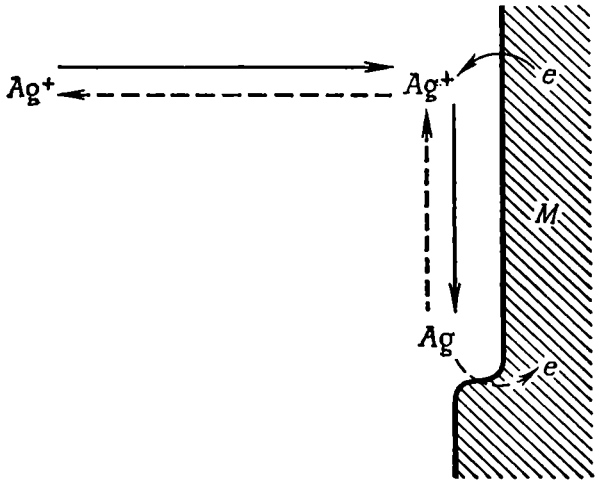

Fig. 13.3. Schematic representation of the electrode reaction of deposition and dissolution of silver: $Ag^+ + e = Ag$. The solid arrow indicates the forward process and the dashed arrow, the reverse process

ions acquire electrons, and are dehydrated and transformed into adsorbed silver atoms. While moving on the electrode surface, these silver atoms seek the most energetically advantageous site to continue the building-up of the silver crystal lattice and become attached to this site. It may be assumed, alternatively, that while discharging at definite portions of the electrode surface the adsorbed (and possibly also partly dehydrated) silver ions are simultaneously incorporated into the crystal lattice.

If the cathodic deposition of silver occurs from a solution of its complex salt (instead of a simple salt), say, from a cyanide electrolyte, the electrode process will be more complicated. Indeed, suppose (in line with experiment) that the silver ions are present in the chosen electrolyte in the form of $Ag(CN)_2^-$ anions. In this case the

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[1] This stage following the discharge act is a heterogeneous (surface) chemical reaction, the rate of which depends on the catalytic properties of the electrode.

discharging process may take one or more of the following paths:

$$\text{I. } Ag(CN)_2^- + e = [Ag] + 2CN^-$$
$$\text{II. (a) } Ag(CN)_2^- = AgCN + CN^-$$
$$\text{(b) } AgCN + e = [Ag] + CN^-$$
$$\text{III. (a) } Ag(CN)_2^- = AgCN + CN^-$$
$$\text{(b) } AgCN = Ag^+ + CN^-$$
$$\text{(c) } Ag^+ + e = [Ag]$$

Path I is a direct discharge of the complex ion on the electrode; it may be broken down into the same principal steps as the discharge of hydrated silver ions (see Fig. 13.3). However, in contrast to the deposition of silver from simple ions, anions instead of cations are discharged in this case and hence the effect of the potential and charge of the electrode on the discharge act must be different. Besides, the discharging process gives rise to excess cyanide ions and, along with the ion transfer to the electrode, there appears another step, the removal of CN^- ions from the electrode surface.

Paths II and III involve partial or complete dissociation of the complex ion, i.e., a purely chemical step taking place in the bulk of the solution. The homogeneous chemical reaction produces particles which are discharged at the electrode, i.e., this reaction precedes the discharge step. Path II is characterized by the discharge of neutral particles, and path III by the occurrence of two purely chemical steps; the final step (b) of path III must proceed according to the scheme shown in Fig. 13.3. These two paths also require the removal of excess CN^- ions from the electrode surface.

13.1.3. CLASSIFICATION OF POLARIZATION PHENOMENA

The examples just discussed do not cover all diverse types of electrode processes. Nevertheless, they give a sufficiently clear idea of the nature of the steps constituting the overall electrode process and can be used as a basis for classifying polarization phenomena. It should be noted that, although the kinetics of electrode processes underlies practically all industrial applications of electrochemistry and is therefore the central topic which is being most thoroughly elaborated by electrochemists, there is as yet no generally accepted and unified terminology in this field, in contrast to the theory of solutions (ionics, as it is sometimes called). In this connection, the nomenclature proposed by Bonhoeffer, Gerischer, and Vetter in 1950 and thoroughly elaborated by Vetter in 1961 is of interest. The classification of the processes and phenomena treated by electrode kinetics, which is adopted in this book, is consistent with the terminology traditionally used in the Soviet electrochemical

literature. At the same time it includes some elements of the nomenclature proposed by Bonhoeffer and his coworkers.

By the net or overall electrode reaction is meant the entire process of transformation of initial substances (reactants) into final products under the effect of an electric current. For example, the overall cathodic reaction in the deposition of metallic silver from the complex cyanide ion $Ag(CN)_2^-$ should be written as follows:

$$Ag(CN)_2^- + e = [Ag] + 2CN^-$$

Individual or partial electrode reactions correspond to chemical (electrochemical) transformations which combine in the overall electrode reaction[1]. If the cathodic deposition of metallic silver from the cyanide complex proceeds by path I, the partial electrode reaction will coincide with the net reaction. If the same process occurs according to path II or III, the overall electrode reaction will be composed of two or three partial reactions, respectively. At least one of the partial reactions must involve electrons, i.e., the gain or loss of electrons by the reactants. The electroreduction (or oxidation) of polyvalent particles may involve several discharge or ionization steps. In view of this, a distinction should be made in the general case between the number of electrons z participating in the overall reaction and the number of electrons z_i taking part in the ith partial reaction.

The electrode polarization $\Delta\varepsilon$ is the deviation of the operating potential (i.e., the potential in the presence of a current) from its equilibrium ε_r or stationary ε_s (in the absence of an external current) value irrespective of the cause responsible for this deviation. Since the potential is displaced to the negative side when a cathodic current is imposed upon the cell and to the positive side when an anodic current is applied, the cathodic polarization is always negative

$$\Delta\varepsilon_c = \varepsilon_i - \varepsilon_r < 0$$

or

$$\Delta\varepsilon_c = \varepsilon_i - \varepsilon_s < 0$$

and the anodic polarization always positive

$$\Delta\varepsilon_a = \varepsilon_i - \varepsilon_r > 0$$

or

$$\Delta\varepsilon_a = \varepsilon_i - \varepsilon_s > 0$$

While no doubt arises as regards the sign of the electrode polarization, the question of which sign should be assigned to the cathodic i_c

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[1] The sum of overall electrode reactions for the two electrodes of a particular electrochemical system yields the overall reaction of the system as a whole. Its equation does not include electrons since each of the two electrode reactions involves the same number of electrons, but while at one electrode electrons are accepted by particles ($z_c = z$), at the other they are lost ($z_a = -z$).

or anodic i_a current has not yet been resolved unambiguously. In accord with the spirit of the Stockholm convention on electrode potentials the cathodic current is considered positive and the anodic current negative.

As noted earlier, the rate-determining step (rds) of the overall electrode process is called the inhibited or limiting step. The slow rate of any step is directly responsible for electrode polarization. If the nature of the inhibited step, which is the cause of the polarization, is known, the term electrode overpotential or simply overpotential η is preferred to polarization.

Thus, the overpotential is an electrode polarization caused by the retarded occurrence of quite a definite step of the net electrode reaction. The term overpotential is very often used in combination with the name of the principal reactant of the reaction the polarization of which is being studied. For example, the terms hydrogen overpotential and metal overpotential mean that one is speaking of the polarization specific for a given reaction and not of the diffusion overpotential.

There are various types of overpotential, depending on the nature of the retarded reaction step. As follows from the above examples, one of the necessary steps of any electrode process is the transport of the reactants to and from the electrode-electrolyte interface. If this step proceeds slowly, i.e., is inhibited, the concentrations (or activities) of all or some of the reactants near the electrode will change as compared with their initial concentrations (or activities) owing to the passage of a current. Since the electrode potential is governed by the solution composition near the electrode surface, the change of the solution composition will alter the potential, i.e., the electrode will become polarized. The slow rate of a purely chemical reaction preceding or following the act of discharging also results in a change in the activities (or concentrations) of the reactants near the electrode surface, which causes the corresponding changes in the electrode potential, i.e., the polarization of the electrode. The polarization arising from the retarded ion transport and chemical transformation steps may be called the concentration polarization $\Delta\varepsilon_c$. A special case of concentration polarization where all the steps of the electrode process, except the transport of reactants, proceed reversibly corresponds to the transport overpotential or (less rigorously) to the diffusion overpotential η_d. Another special case of concentration polarization occurs when all the steps of the electrode reaction, except the chemical transformation, proceed reversibly. This type of concentration polarization is called the *chemical* η_{ch} or *reaction overpotential* η_r.

As already noted, any electrode process involves at least one step associated with the transfer of charges across the electrode-electrolyte interface. The electrode polarization caused by the slow rate

of this step may be called the electrochemical overpotential η_e because it is precisely this charge-transfer process that is the electrochemical act proper. This type of overpotential is often also called the retarded discharge or transition (or electron-transfer) overpotential. And, finally, the overpotential observed when the inhibited step is the incorporation of metallic ions into the crystal lattice, or their separation from it, and also when the slow step is the transformation of one modification (less stable) into another (more stable under given conditions) may be called the *phase overpotential* η_{ph}. Changes in the concentration taking place near the electrode surface are but of secondary importance for the occurrence of the electrochemical and phase overpotentials. Of much greater importance in this case is the change in the activation energy of the corresponding process. The electrochemical and phase overpotentials are therefore often collectively termed the *activation polarization* $\Delta\varepsilon_{ac}$. In the general case, the deviation of the actual operating electrode potential from the equilibrium value is the result of superposition of all the types of overpotential, i.e.,

$$\Delta\varepsilon_i = \eta_d + \eta_r + \eta_e + \eta_{ph} \tag{13.7}$$

or

$$\Delta\varepsilon_i = \Delta\varepsilon_c + \Delta\varepsilon_{ac} \tag{13.8}$$

There are, however, such electrode processes and conditions in which one type of overpotential predominates.

The subdivision of polarization into concentration and activation polarizations is somewhat arbitrary. Thus, the phase overpotential referred to activation polarization is essentially dependent on the concentration of intermediate particles and in this sense it may be related to concentration polarization. The rate of the purely chemical reaction step is also determined by the corresponding value of the activation energy. The chemical or reaction overpotential defined above as a special case of concentration polarization may also be included, on certain grounds, in the activation polarization. The overpotential caused by the slow chemical reaction step is therefore a sort of an intermediate link between the concentration and activation polarization.

CHAPTER 14
Concentration Polarization

The slow rates of transport and purely chemical transformation lead to changes in the concentration of the reactants near the electrode[1]. This results in a change in the equilibrium electrode potential, thus giving rise to concentration polarization. Besides, the concentration of the particles taking part in other steps of the electrode process (say, in the discharge step) also undergoes a change, a fact that should be taken into account in considering the kinetics of these steps. The effect of concentration polarization on the kinetics of the entire electrode process and on the magnitude of electrode potential in the presence of current may be disregarded only at low rates of the electrochemical reaction, i. e., at small current densities. Conversely, at high current densities the transport step may control the rate of the overall electrode process.

14.1. DIFFUSION OVERPOTENTIAL

14.1.1. THE CONCEPT OF DIFFUSION OVERPOTENTIAL

The diffusion overpotential η_d is the deviation of the electrode potential under the applied current from its equilibrium value caused by the slow occurrence of the transport of reactants to or from the electrode surface.

If the other steps of the electrode reaction proceed reversibly or at rates incomparably higher than the rate of the transport step, then all the changes in the electrode potential due to the passage of a current i may be identified with diffusion overpotential. In this case Eq. (13.6) becomes

$$\eta_d = \varepsilon_i - \varepsilon_r \tag{14.1}$$

Here the shift of the potential from the reversible value however results exclusively from concentration changes, and the irreversible

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[1] The expression "near the electrode" refers to the layer of solution which is adjacent to the electrode surface and is directly drawn into the charge-exchange between electrode and solution, i.e., determines the electrode potential.

electrode potential ε_i may therefore be regarded as a new value of the equilibrium potential, ε_r', which differs from ε_r only in that now it corresponds to other concentrations or, more precisely, other activities of the reactants. In other words, the diffusion overpotential, as a quasi-equilibrium phenomenon, may be described by purely thermodynamic means. In this case only the initial and final states of a system are essential, while the transient stage and the mechanism underlying this transition are of no significance. Suppose that the following reaction proceeds at the electrode:

$$\nu_A A + \nu_B B + \ldots + zF = \nu_L L + \nu_M M + \ldots \qquad (14.2)$$

the activities of the respective substances being equal to a_A, a_B, a_L and a_M. The electrode potential will then be given by the equation

$$\varepsilon_r = \varepsilon_0 + \frac{RT}{zF} \ln \frac{a_A^{\nu_A} a_B^{\nu_B}}{a_L^{\nu_L} a_M^{\nu_M}} \qquad (14.3)$$

When a current i is imposed on the system, the solution composition near the electrode begins to change and after a definite period of time, when a stationary state is reached, the activities of the reactants in the solution layer in the immediate vicinity of the electrode assume new, constant values, a_A', a_B', a_L' and a_M'. The equilibrium potential ε_r' will now be described by the following equation

$$\varepsilon_r' = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_A'^{\nu_A} a_B'^{\nu_B}}{a_L'^{\nu_L} a_M'^{\nu_M}} \qquad (14.4)$$

Substitution of Eqs. (14.43) and (14.4) into Eq. (14.1) yields the general equation for diffusion overpotential:

$$\eta_d = \varepsilon_i - \varepsilon_r = \varepsilon_r' - \varepsilon_r = \frac{RT}{zF} \ln \frac{(a_A'/a_A)^{\nu_A} (a_B'/a_B)^{\nu_B}}{(a_L'/a_L)^{\nu_L} (a_M'/a_M)^{\nu_M}} \qquad (14.5)$$

If the stoichiometric numbers of the reactants are assigned positive, and those of the products negative values, Eq. (14.5) may be rewritten in the form

$$\eta_d = \frac{RT}{zF} \Sigma \nu_j \ln \frac{a_j'}{a_j} \qquad (14.6)$$

Thus, in order to write the equation for diffusion overpotential it is only necessary to know the overall electrode reaction. For example, for the reaction

$$Fe^{3+} + e = Fe^{2+} \qquad (14.7)$$

Eq. (14.5) simplifies to

$$\eta_d = \frac{RT}{zF} \ln \frac{a'_{Fe^{3+}}/a_{Fe^{3+}}}{a'_{Fe^{2+}}/a_{Fe^{2+}}} \tag{14.8}$$

In the cathodic process (reduction of ferric ions to ferrous ions) $a'_{Fe^{3+}} < a_{Fe^{3+}}$, $a'_{Fe^{2+}} > a_{Fe^{2+}}$ and the cathodic diffusion overpotential is negative. In the anodic process (oxidation of ferrous ions to ferric ions) $a'_{Fe^{3+}} > a_{Fe^{3+}}$, $a'_{Fe^{2+}} < a_{Fe^{2+}}$, and the anodic diffusion overpotential is positive.

The diffusion overpotential accompanying the reaction

$$Ag^+ + e = [Ag] \tag{14.9}$$

is given by the equation

$$\eta_d = \frac{RT}{F} \ln \frac{a'_{Ag^+}}{a_{Ag^+}} \tag{14.10}$$

and that associated with the reaction involving complex silver ions

$$Ag(CN)_2^- + e = [Ag] + 2CN^- \tag{14.11}$$

is described by the following equation

$$\eta_d = \frac{RT}{F} \ln \frac{a'_{Ag(CN)_2^-}/a_{Ag(CN)_2^-}}{(a'_{CN^-}/a_{CN^-})^2} \tag{14.12}$$

In all these cases the change in the electrolyte composition near the electrode will be such that the value of diffusion overpotential will be negative during cathodic polarization and positive during anodic polarization. For instance, when reaction (14.9) proceeds in the cathodic direction, the solution near the electrode is depleted in silver ions ($a'_{Ag^+} < a_{Ag^+}$ and $\eta_{d(c)} < 0$). Conversely, if the same reaction proceeds towards the anode, the concentration of silver ions near the electrode increases ($a'_{Ag^+} > a_{Ag^+}$ and $\eta_{d(a)} > 0$). Such changes in the solution composition were first experimentally observed by Samartsev (1932-34), who used a modified interferometric method. Later other methods were also used to study the state of the electrolyte near the electrode as a function of the polarizing current. Among these methods were so-called schlieren microscopy and observations of suspended particles whose distribution is dependent on the density of the solution and hence on its concentration and also on the pattern of motion of the liquid. The experimental evidence so obtained served as a qualitative confirmation of the general equation for diffusion overpotential. It should be stressed however that Eqs. (14.5) and (14.6) have been derived on the basis of general thermodynamic principles and cannot therefore reflect the kinetics of the process, i.e., they do not enable one to establish

a relation between the diffusion overpotential (a measure of the irreversibility of the process) and the current intensity (a measure of its rate). To solve this problem, certain assumptions have to be made as to the nature of the transport step and the structure of the boundary layer within which this process takes place.

The transport of reactants to the electrode surface and from the zone of the electrode reaction in the absence of intermediate chemical transformation is accomplished in three ways: *migration*, *molecular diffusion* and *convection*.

Migration or *ionic conduction* is the movement, or drift, of ions (or other charged particles) under the influence of an electric field gradient (potential gradient) $-d\psi/dx$ arising in the electrolyte on passage of a current through the electrochemical system. The migration of ions was discussed in Chapter 4, where it was shown that the direction of the movement of an ion j in an electric field is determined by the sign of its charge z_j and the migrational velocity depends on its transport number t_j under given conditions. Since $t_j = \lambda/\Sigma\lambda_j$, it follows that in the presence of an excess of extraneous ions (i.e., an indifferent electrolyte which does not participate directly in the electrode reaction) the transport number of the given ionic species tends to zero, and the contribution of ionic migration to the overall process of transport may be neglected.

Molecular diffusion is the displacement of particles under the action of a chemical-potential gradient $-d\mu/dx$ or, loosely speaking, a concentration gradient $-dc/dx$, arising in the solution owing to its qualitative and quantitative inhomogeneity. Molecular diffusion has already been considered in Chapter 6, where Fick's laws describing this process were derived.

Convective diffusion is the transport of solute particles together with the stream of a moving liquid. The flow of the liquid either occurs spontaneously, if there is a difference in the density of the solution in its different parts, i.e., if there is a density gradient $-d\rho/dx$ (natural convection), or is induced by stirring and circulation (forced convection).

Migration, diffusion and convection may be superimposed in different ways during the transport process, depending on the direction of the reaction (cathodic or anodic), the charge sign of the particles involved (cations, anions, or uncharged entities) and their role in the electrode reaction (whether they are reactants or products, participate directly in the charge exchange with the electrode or indirectly, as, for example, ligands of complex particles).

Figure 14.1 shows schematically how these three transport processes are superimposed during the cathodic reduction of cations, anions and molecules in solutions containing no excess of extraneous electrolyte. In the reduction of positively charged particles (Fig. 14.1*a*) their transport towards the cathode is accomplished by migration,

diffusion and convection, they all occurring in the same direction. In the reduction of anions (Fig. 14.1*b*) they are transported to the cathode by diffusion and convection and removed from the electrode surface by migration. In the reduction of uncharged particles (Fig. 14.1*c*) no migration occurs. In anodic oxidation the transport

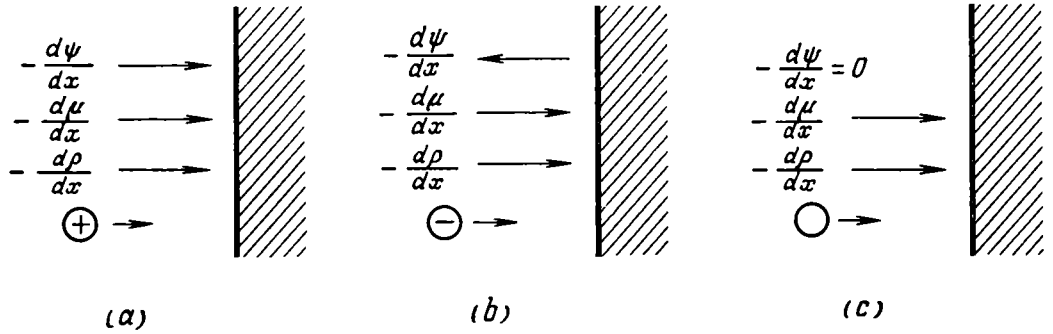

Fig. 14.1. Transport of particles to the cathode surface in the absence of extraneous (indifferent) electrolyte:
a—cations; *b*—anions; *c*—uncharged particles

of cations to the electrode is opposed by migration, and the anions are transported by migration, diffusion and convection; in the case of oxidation of organic substances only diffusion and convection are involved in the transport process.

14.1.2. THE THEORY OF DIFFUSION OVERPOTENTIAL NEGLECTING CONVECTION

In the first quantitative theory of diffusion overpotential developed mainly by Nernst and Brünner at the turn of the century (1888-1904) only the migration and diffusion of ions are taken into account.

In this theory it is further assumed that all the changes in the electrolyte composition are confined to a narrow solution layer adjacent to the electrode, i.e., to the diffusion layer δ. This layer is supposed to be stagnant. It is not involved in the motion of the liquid taking place within a given system. The Nernst-Brünner diffusion-layer model is schematically shown in Fig. 14.2. The change in the concentration of the electrolyte, one of the ions of which takes part in the electrode reaction, occurs in this layer linearly from a certain value c_0, corresponding to the bulk concentration, to c near the electrode (in Fig. 14.2*a*, to c_c since a cathodic process is considered). Thus, the concentration gradient determining the diffusion rate is equal to $(c_0 - c_c)/\delta$. Finally, in this theory it is tacitly assumed that the concentrations and activities are equal (although no explicit assumption was made by the authors of the

theory since the concept of activity was unknown at the time) and that the transport numbers are independent of the solution composition. The latter assumption is justified only in the case of solutions containing a binary electrolyte where the mobilities of the component ionic species are almost equal (see Tables 4.2 and 4.3). The

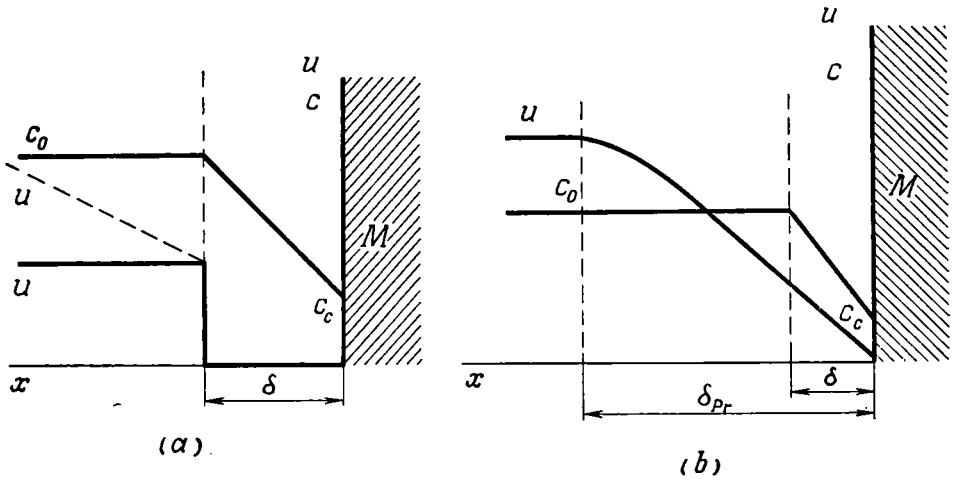

Fig. 14.2. Variation of liquid velocity u and concentration c near the cathode surface:

a—according to Nernst and Brünner; *b*—according to Levich

basic propositions of the Nernst-Brünner theory of diffusion overpotential may therefore be conveniently illustrated by considering the following system

$$Ag/AgNO_3/Ag$$

made up of two silver electrodes and a solution of silver nitrate—a binary electrolyte, the transport numbers of whose components are almost independent of concentration.

Suppose that a current flows through the electrolyte of the chosen system from left to right. The left electrode is then the anode, and silver dissolves, forming ions, while the right electrode is the cathode at which silver ions are discharged to form metallic silver. If a quantity of electricity equal to one faraday is passed through the system and a current efficiency of 100 per cent is maintained, one gram-ion of silver ions will be transported from the solution to the electrode. The time τ taken by this process is given by the equation

$$\tau = \frac{F}{I}$$

Hence, as a result of the electrochemical process the concentration of silver ions near the cathode decreases at the rate

$$-\frac{1}{\tau} = -\frac{I}{F}$$

At the same time, one faraday of electricity will carry t_+ gram-ions of silver from the solution to the electrode. The rate of increase of the silver-ion concentration near the cathode owing to transport at a current intensity I is equal to

$$\frac{t_+}{\tau} = t_+ \frac{I}{F}$$

Usually $t_j < 1$ and the loss of silver ions as a result of discharge cannot be compensated by migration. The associated decrease of the concentration down to c_c in the region around the cathode as compared with the concentration c_0 in the bulk of the solution sets up a concentration gradient and results in diffusion to the electrode at the rate

$$\Delta_+ \Omega \frac{c_0 - c_c}{\delta}$$

where Δ_+ = diffusion coefficient of silver ions
Ω = macrosurface area of the electrode-electrolyte interface equal to the geometrical dimensions of the electrode.

When a stationary state is reached, a state to which there corresponds quite a definite concentration c_c dependent on the current intensity, the rates of transport of silver ions from and to the near-cathode layer are equalized, i.e.,

$$-\frac{I}{F} + t_+ \frac{I}{F} + \Delta_+ \Omega \frac{c_0 - c_c}{\delta} = 0 \qquad (14.13)$$

Using Eq. (14.13), one can find the concentration c_c near the cathode at a current intensity I or at a current density $i = I/\Omega$:

$$c_c = c_0 - \frac{(1 - t_+)\,\delta}{F \Delta_+ \Omega} I = c_0 - \frac{(1 - t_+)\,\delta}{F \Delta_+} i \qquad (14.14)$$

Equation (14.13) can also be used to calculate the current density i, which corresponds to the concentration c_c in the region around the cathode:

$$i = F \Delta_+ \frac{1}{(1 - t_+)} \cdot \frac{c_0 - c_c}{\delta} \qquad (14.15)$$

Substitution of the values of $c_c = a'_{Ag^+}/f_c$ from Eq. (14.14) into Eq. (14.10) and replacement of a_{Ag^+} by $c_0 f_0$ gives

$$_c\eta_d = \frac{RT}{F} \ln \left[1 - \frac{(1 - t_+)\,\delta}{F \Delta_+ c_0} i \right] \frac{f_c}{f_0}$$

or, at $f_c = f_0$, in accordance with the assumption made earlier,

$$_c\eta_d = \frac{RT}{F} \ln \left[1 - \frac{(1 - t_+)\,\delta}{F \Delta_+ c_0} i \right] \qquad (14.16)$$

For a binary electrolyte, MA, whose ionic charges are equal to z Eq. (14.16) may be written thus

$$_c\eta_d = \frac{RT}{zF} \ln \left[1 - \frac{(1-t_+)\,\delta}{zF\Delta_+ c_0}\, i \right] \tag{14.17}$$

Analogous reasoning for the anodic process leads to the equations

$$_a\eta_d = \frac{RT}{F} \ln \left[1 + \frac{(1-t_+)\,\delta}{F\Delta_+ c_0}\, i \right] \tag{14.18}$$

for the formation of univalent ions and

$$_a\eta_d = \frac{RT}{zF} \ln \left[1 + \frac{(1-t_+)\,\delta}{zF\Delta_+ c_0}\, i \right] \tag{14.19}$$

for the formation of cations of charge z.

Taking into account that in the second term of the logarithmic expression the factor before the current density is independent of the latter and is constant for a given electrode reaction and temperature, Eqs. (14.16) to (14.19) may be rewritten in the form

$$\eta_d = \frac{RT}{zF} \ln (1 \pm k_d i) \tag{14.20}$$

where

$$k_d = \frac{(1-t_+)\,\delta}{zF\Delta_+ c_0} \tag{14.21}$$

In Eq. (14.20) the minus sign refers to the cathodic and the plus sign to the anodic process.

By using electrode balances one can obtain equations relating the diffusion overpotential to the current density for more complicated electrode reactions as well. An expression analogous to Eq. (14.20) obtains for each jth participant of the electrode reaction; from the general equation for the diffusion overpotential (14.6) it clearly follows that here the logarithmic expression is raised to a power of ν_j corresponding to the stoichiometric number of the given ionic species, i.e., in the general case

$$\eta_d = \frac{RT}{zF} \Sigma \nu_j \ln (1 \pm {}_j k_d i) \tag{14.22}$$

The right-hand side of Eq. (14.22) may be expanded into a series

$$\eta_d = \frac{RT}{zF} \Sigma \nu_j \ln (1 \pm {}_j k_d i) = \pm \frac{RT}{zF} \Sigma \nu_j\, {}_j k_d i - $$

$$- \frac{RT}{zF} \Sigma \nu_j ({}_j k_d i)^2 \frac{1}{2} \pm \frac{RT}{zF} \Sigma \nu_j ({}_j k_d i)^3 \frac{1}{3} - \ldots$$

and as $\eta_d \to 0$ and $i \to 0$ all the terms higher than the first may be eliminated:

$$\lim_{\eta_d \to 0;\ i \to 0} \eta_d = \pm \frac{RT}{zF} \Sigma \nu_j {}_j k_d i \tag{14.23}$$

In this case the diffusion overpotential is a linear function of the current density. The derivative

$$\left(\frac{d\eta_d}{di}\right)_{\substack{\eta_d \to 0 \\ i \to 0}} = \pm \frac{RT}{zF} \Sigma \nu_j {}_j k_d = R_d \tag{14.24}$$

has the dimensions of the resistance and is called the *polarization resistance* R_d at diffusion overpotential; it is determined by the stoichiometry of the electrode reaction and by the limiting current density.

With increasing cathodic current density the diffusion overpotential will gradually increase until the product ${}_j k_d i$ approaches unity. Under these conditions even an insignificant additional increase in the current density shifts the potential in the negative direction and at ${}_j k_d i = 1$ the cathodic diffusion overpotential will adopt an infinitely large negative value, ${}_c\eta_d = -\infty$. The current density corresponding to these conditions is called the *limiting cathodic diffusion current density*:

$${}_d i_{l(j)} = \frac{1}{{}_j k_d} \tag{14.25}$$

The limiting cathodic current density is reached when the near-cathode electrolyte layer is completely depleted in the ions, i.e., at $c_c = 0$[1]. This follows from a comparison of the equation

$${}_d i_{l(j)} = \frac{1}{{}_j k_d} = zF\Delta_+ \frac{1}{(1-t_+)} \frac{c_0}{\delta} \tag{14.26}$$

resulting from Eqs. (14.21) and (14.25) with Eq. (14.15) rewritten for ions of valency z as follows:

$$i_{d(j)} = zF\Delta_+ \frac{1}{(1-t_+)} \frac{c_0 - c_c}{\delta} \tag{14.27}$$

It is not difficult to see that at the limiting current density the concentration gradient

$$-\frac{dc}{dx} = \frac{c_0 - c_c}{\delta}$$

and, consequently, the diffusion rate reach the highest value. Further rise of the current density is impossible, and so the diffusion limits the rate of the electrode reaction. The shift of the potential observed at the limiting current density may however induce a new cathodic reaction, the reversible potential of which is more electronegative than that of the initial reaction, and thus further increase of the current density becomes possible.

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[1] This inference can also be made on the basis of the general equation for the diffusion overpotential (14.6). Indeed, if in the numerator of Eq. (14.6) the activity of any one of the reacting species is taken as equal to zero, the overpotential will assume an infinitely high negative value.

From Eqs. (14.26) and (14.27) it follows that

$$\frac{d^{i_{(c)}}}{d^{i_{l(c)}}} = \frac{c_0 - c_c}{c_0} = 1 - \frac{c_c}{c_0} \tag{14.28}$$

or

$$\frac{c_c}{c_0} = 1 - \frac{d^{i_{(c)}}}{d^{i_{l(c)}}} \tag{14.29}$$

The use of these relations in conjunction with the basic equation (14.6) enables one to obtain in a straightforward way the relationship between diffusion overpotential and the current density. Clearly, in place of Eq. (14.20), one can write for the cathodic process:

$$_c\eta_d = \frac{RT}{zF} \ln \left(1 - \frac{i}{d^{i_{l(c)}}}\right) \tag{14.30}$$

which permits calculation of the diffusion overpotential η at any current density i if the limiting current density $_d i_{l(c)}$ is known.

The equation for the anodic diffusion overpotential in its simplest form

$$_a\eta_d = \frac{RT}{zF} \ln (1 + k_d i)$$

shows that $_a\eta_d$ increases monotonically with increasing current density and therefore, in contrast to the cathodic process, in this case the limiting current density should not be reached, as might appear at first glance. Experiment shows however that for anodic dissolution of a metal the polarization curve exhibits a section of limiting current and sometimes, after a definite potential is attained, even a fall of the current density. One of the causes of this discrepancy between theory and experiment is associated with the assumptions made in considering electrode reactions, in particular, with the assumption that free ions are formed in anodic dissolution of a metal, e.g. silver. In actual fact all the ions are more or less hydrated. With account taken of the hydration of ions, reaction (14.9) must be rewritten in the following form

$$Ag^+_{aq} + e = [Ag] + n_h H_2O \tag{14.31}$$

where Ag^+_{aq} are hydrated (aquated) silver ions, the primary hydration sheath of which contains n_h water molecules. The general equation of the diffusion overpotential (14.5) for this particular case should now be written thus

$$\eta_d = \frac{RT}{zF} \ln \frac{a'_{Ag^+(aq)}/a_{Ag^+(aq)}}{(a'_{H_2O}/a_{H_2O})^{n_h}} \tag{14.32}$$

and electrode balances should be drawn up for each of the reactants—the Ag^+_{aq} ions and water molecules. For silver ions the balances for

reactions (14.9) and (14.31) are the same. In drawing up a balance for water molecules one should take into account only their binding to ions in the course of the electrode reaction proceeding at the rate

$$-n_h \cdot \frac{I}{F}$$

and diffusion, the rate of which is equal to

$$\Delta_{H_2O}\Omega \frac{c^0_{H_2O} - c_{H_2O}}{\delta}$$

Being uncharged particles, water molecules do not migrate and their transport together with the silver and nitrate ions may be ignored at a first approximation. When a stationary state is attained,

$$-n_h \frac{I}{F} + \Delta_{H_2O}\Omega \frac{c^0_{H_2O} - c_{H_2O}}{\delta} = 0$$

or

$$c_{H_2O} = c^0_{H_2O} - \frac{n_h \delta}{F\Delta_{H_2O}} i \tag{14.33}$$

Substitution of ${}_a c_{Ag^+(aq)} = c^0_{Ag^+(aq)} + \frac{(1-t_+)}{F\Delta_+} i$ for $a'_{Ag^+(aq)}$ and of c_{H_2O} from Eq. (14.33) for a'_{H_2O} in Eq. (14.32) yields

$${}_a\eta_d = \frac{RT}{F} \ln \frac{\left[1 + \frac{(1-t_+)\delta}{F\Delta_+ c^0_{Ag^+(aq)}} i\right]}{\left(1 - \frac{n_h \delta}{F\Delta_{H_2O} c^0_{H_2O}} i\right)^{n_h}} \tag{14.34}$$

It follows from Eq. (14.34) that when increasing the current density can reach a limiting value corresponding to

$${}_d i_{l(a)} = F\Delta_{H_2O} \frac{c^0_{H_2O}}{\delta n_h} \tag{14.35}$$

This limiting value is attained the sooner the higher the hydration number n_h of the aquated silver ions formed and it must correspond to such a state of the electrolyte in the region around the anode when practically all the water is bound to the ions.

Similarly, for the reaction

$$Ag(CN)_2^- + e = [Ag] + 2CN^-$$

proceeding from right to left the following equation can be obtained:

$${}_a\eta_d = \frac{RT}{F} \ln \frac{1 + k_a i}{\left(1 - \frac{i}{{}_d i_{l(a)}}\right)^2} \tag{14.36}$$

which also indicates that the anodic limiting current density can be attained. Its magnitude

$$i_{d(a)} = \frac{F\Delta_- c_0}{2(1-t_-)\delta} \tag{14.37}$$

corresponds to the complete depletion of the near-anode layer in CN^- ions.

It should be pointed out however that often, even before the limiting current density is attained, the concentration of the resulting substance in the region around the anode reaches its solubility limit, c_s, i.e., the solution becomes saturated. Further increase of the concentration is impossible, the concentration gradient attains its maximum value, $(c_s - c_0)/\delta$, and consequently the anodic current density cannot be expected to increase either. The metal salt may begin to deposit from the saturated solution on to the electrode surface. Since the electrical conductance of most solid compounds is small, there will be a noticeable fall of the potential in the deposited salt. The appearance of an apparent limiting current density is often due to the formation of surface compounds with the participation of oxygen. In all these cases the shift of the potential to the positive side may even be accompanied by a decrease in the anodic current density. These phenomena constitute the various forms of transition of a metal into the so-called passive state.

Thus, the diffusion overpotential is determined primarily by the limiting current density i_d or by the constant k_d. According to the Nernst-Brünner theory and to Eq. (14.26), the limiting current density depends mainly on the diffusion coefficient of the corresponding particles, Δ_j, their charge z_j and initial concentration c_j^0 (or, what is the same thing, their concentration beyond the diffusion layer) and the diffusion-layer thickness δ. As has already been noted, the transport numbers of a given ionic species, t_j, can be reduced to zero; besides, no migration occurs in the case of uncharged particles. The diffusion coefficient can either be calculated or taken from experimental data; the initial concentration c^0 can also be easily determined. The least definite quantity is the diffusion-layer thickness which cannot be calculated within the framework of the Nernst-Brünner theory. It is determined experimentally, most often from measurements of the limiting current density. Experimental evidence shows that δ depends very little on the solution composition but changes perceptibly when the regime of electrolyte motion is changed. This relationship can be expressed by the empirical formula

$$\delta_\omega = \delta_0 \omega^{-n} \tag{14.38}$$

where ω = angular velocity of the rotating electrode equal to $2\pi m$ (m is the number of revolutions of the rotating-disc electrode per 1 second)

δ_0 = diffusion-layer thickness at an angular velocity equal to unity

n = a number close to 0.5.

The diffusion-layer thickness determined experimentally ranges from 10^{-5} to 10^{-2} cm depending on the rate of agitation. These values of δ are incompatible with the assumption of complete immobility of the solution in the diffusion layer. Indeed, in this case the forces arising between the electrode and the solution and responsible for the retarded motion should have extended over hundreds of thousands of molecular layers, which contradicts all the available evidence on the nature of intermolecular forces and is inconsistent with the results of electrokinetic investigations.

14.1.3. THE THEORY OF DIFFUSION OVERPOTENTIAL COVERING CONVECTIVE DIFFUSION

Despite the obvious drawbacks of the Nernst-Brünner theory—the impossibility of the theoretical calculation of the limiting current density, the physical incongruity of the diffusion-layer model—nearly 40 years elapsed until a new, more perfect theory of the diffusion overpotential was created. Advances in this line have been achieved owing to the application of the basic conceptions of heat and mass transfer, particularly the laws of hydrodynamics, to diffusion phenomena.

This new theory of diffusion overpotential has emerged from the contributions made by many scientists, especially by Levich (1942-1950). The underlying principle of this theory is that the stagnant layer is actually the layer immediately adjacent to the electrode surface and having a thickness of several atomic diameters, i.e., incomparably less than that of the diffusion layer. Both within and beyond the diffusion layer the solution is not at rest. The velocity of its motion (flow rate) changes on approaching the electrode from $u = u_\infty$ in the bulk of the solution to $u = 0$ on the electrode surface. The change of the flow rate occurs in a certain layer called the *boundary layer* δ_b or the *Prandtl layer* δ_{Pr}. The transfer of motion from one layer to another is determined by the kinematic viscosity of the liquid, ν, which is the ratio of its viscosity γ to its density ρ:

$$\nu = \frac{\gamma}{\rho} \tag{14.39}$$

For most solutions ν is of the order of 10^{-2} cm^2 sec^{-1}. The transport of the solute from layer to layer, i.e., its diffusion, is determined by the diffusion coefficient Δ, which is usually of the order of 10^{-5} cm^2 sec^{-1}. Thus, the transfer of motion is more effective than the transport of the solute by diffusion and therefore at comparable values of Δu and Δc the velocity gradient may be lower than the

concentration gradient, i.e., the thickness of the Prandtl layer must be greater than that of the diffusion layer, $\delta_{Pr} > \delta$. It has been shown that these quantities are interrelated by the equation

$$\frac{\delta}{\delta_{Pr}} = \left(\frac{\Delta}{\nu}\right)^{1/3} \tag{14.40}$$

In other words, the diffusion-layer thickness is approximately one-tenth of the Prandtl layer thickness

$$\delta = \left(\frac{\Delta}{\nu}\right)^{1/3} \delta_{Pr} = \left(\frac{10^{-5}}{10^{-2}}\right)^{1/3} \delta_{Pr} = 0.1\delta_{Pr} \tag{14.41}$$

In the layer δ the solution is not at rest, but its flow rate varies linearly, as a first approximation, with distance from the electrode surface.

The relationship between δ and δ_{Pr} and also the variation of u and c with distance from the electrode are shown schematically in Fig. 14.2*b*. The value of δ is governed not only by the velocity of the liquid but also by the geometry of the electrodes and of the system as a whole and by the method employed to induce the flow of the liquid.

For the case of natural convection due to the concentration gradient and hence to the solution density gradient, similar equations have been derived by a number of workers (Levich, Agar, Wagner, and others) for a vertical plate electrode, which is very often encountered in electrochemical practice (e.g. in stationary electrolytic cells, storage batteries):

$$\delta = \frac{1}{k}\left(\frac{\Delta\nu h}{\frac{1}{\rho}\frac{d\rho}{dc}\Delta c g}\right)^{1/4} \tag{14.42}$$

The equations obtained differ slightly only in numerical value of the constant k, which may be taken, on the average, as 0.6. In Eq. (14.42) h is the distance reckoned along the vertical from the lower edge of the electrode (see Fig. 14.3*a*), ρ the density of the solution, g the acceleration due to gravity, and Δc is the difference in concentration within the diffusion layer δ. Equation (14.42) shows, in particular, that for a given system δ is a function of the distance from a given point on the electrode to its lower edge, i.e., a function of the electrode height. With increasing distance from the lower edge the value of δ increases proportionally to h, while the current density and the limiting current density decrease accordingly[1]:

$$_h i_l = zFk\left(\frac{\frac{1}{\delta}\frac{d\rho}{dc}g}{\nu \cdot h}\right)^{1/4} \Delta^{3/4} c^{5/4} \tag{14.43}$$

[1] At the limiting current density $\Delta c = c$ since $c_e = 0$.

From Equation (14.43) it follows that under natural convection the limiting current density, in contrast to the Nernst theory, becomes dependent on the diffusion coefficient to the power of 3/4 and also on the concentration to the power of 5/4. These corollaries from

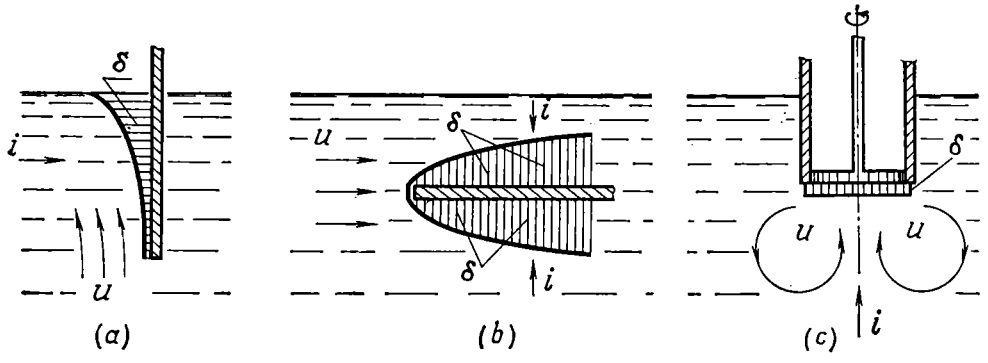

Fig. 14.3. Some practically important cases of convective diffusion:
a—vertical plate (the cathode under conditions of natural convection); *b*—horizontal plate (cathode) along which a liquid flows; *c*—rotating-disc electrode

Eq. (14.43) were confirmed recently by direct experimental observations.

Another special case of importance is the laminar flow of a liquid flowing onto a plate electrode from one side (Fig. 14.3*b*).

In this case, according to Eucken and Levich, ρ is given by the equation

$$\delta = 3x^{1/2}u_{\infty}^{-1/2}\nu^{1/6}\Delta^{1/3} \qquad (14.44)$$

where x = distance along the horizontal from the electrode edge onto which the solution flows

u_{∞} = rate (velocity) of the liquid flow parallel to the electrode plane at an infinitely large distance from it.

Equation (14.44) agrees with the experimentally found relation between the diffusion-layer thickness and the rate of stirring. For the limiting current density at a point x under the given conditions

$$_{x}i_{l} = \frac{1}{3}zFu_{\infty}^{1/2}\nu^{-1/6}\Delta^{2/3}cx^{-1/2} \qquad (14.45)$$

In this case the dependence of limiting current density on diffusion coefficient is also found to be different from that in the Nernst-Brünner theory.

A third case of convective diffusion occurs when a rotating-disc electrode is used (see Fig. 14.3*c*). A specific feature of the rotating-disc electrode (as indicated by Levich) is the constancy of the diffusion-layer thickness at any point of its surface provided that $\delta < r$ (r is the radius of the disc electrode). The equation for the diffusion-

layer thickness under the conditions of laminar flow

$$\delta = 1.61\omega^{-1/2}\nu^{1/6}\Delta^{1/2} \tag{14.46}$$

is therefore valid for any point on the disc electrode and for the electrode as a whole.

The limiting current on the rotating-disc electrode is described by the equation

$$_{d}i_{l} = 0.62zF\omega^{1/2}\nu^{-1/6}\Delta^{1/2}c_0 \tag{14.47}$$

Still another important case—the dropping mercury electrode—will be treated later on in the section on polarography.

The conditions of convective diffusion are found to be much more complicated in the case of turbulent flow. No sufficiently detailed quantitative theory exists so far and the discussion of this question would hardly be expedient within the scope of this textbook.

All the equations given in the present chapter refer to the diffusion overpotential under stationary conditions, i.e., when the concentration gradient is time-invariant and the diffusion-layer thickness has attained a constant value. The time required for such a stationary state to be reached is very short, but it is finite and depends on a number of factors, primarily on the current density and the electrolyte concentration. The treatment of the processes of nonstationary diffusion is based on Fick's second law:

$$\left(\frac{\partial c}{\partial t}\right)_x = \Delta\left(\frac{\partial^2 c}{\partial x^2}\right)_t \tag{14.48}$$

The use of this equation, i.e., its solution for the case under consideration is impossible without formulation of the boundary conditions, which may be different depending on the nature of the system under study and the procedure used for carrying out the electrode reaction (for example, at a constant current, under galvanostatic conditions, or at a constant potential, under potentiostatic conditions). A fundamentally correct way for solving the differential equation (14.48) without taking into account convective diffusion was suggested at the end of the nineteenth century (Sokolov and Weber). Later this problem was treated in the works of many scientists—Sand, Cottrell, Agar, Bowden, and others. It has recently been the subject of the original investigations carried out by Gorbachev and his coworkers, especially by Khlopanov. Equations describing the process of nonstationary diffusion are, as a rule, rather sophisticated. An example is the formula derived by Rosebrugh and Lash-Miller and referring to galvanostatic conditions:

$$\eta_d = \frac{RT}{zF}\Sigma\nu_j \ln\left[1-(1-p)\frac{i}{d^{i_l}}\right] \tag{14.49}$$

where

$$p = \frac{8}{\Pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \exp\left\{-\frac{(2m-1)^2}{4t^0} t\right\} \qquad (14.50)$$

and

$$t^0 = \frac{\delta^2}{\Pi^2 \Delta}$$

At a sufficiently large t ($t \to \infty$) the value of $p \to 0$ tends to zero and Eq. (14.49) is transformed into the stationary diffusion equation (14.22):

$$\eta_d = \frac{RT}{zF} \Sigma \nu_j \ln\left(1 - \frac{i}{j i_l}\right)$$

14.1.4. THE IMPORTANCE OF DIFFUSION OVERPOTENTIAL PHENOMENA FOR ELECTROCHEMICAL PROCESSES

The equations describing diffusion overpotential are based on the assumption of a thermodynamic equilibrium being maintained between electrode and electrolyte. They follow from the Nernst formula for reversible potential. Thus, a study of diffusion overpotential can yield no additional information on the actual path of the electrode reaction or the steps constituting this reaction. At the same time, the application of experimental techniques based on diffusion overpotential phenomena—the dropping mercury electrode (see Chapter 18) and rotating-disc electrode—enables determination of many quantities playing an important role in the kinetics of electrode processes and in electrochemistry in general. For example, the measurement of limiting current on the disc electrode makes it possible to calculate the diffusion coefficients of individual ions, Δ_j, to find out the number of electrons z participating in an electrode reaction and to ascertain whether diffusion is the sole limiting step. A study of diffusion overpotential phenomena is of still greater importance for effective solution of numerous problems in industrial electrochemistry. Indeed, the existence of the limiting diffusion current density restricts the possibility of speeding up electrochemical processes. The diffusion overpotential theory enables one to map out ways for increasing the limiting current density or, in other words, to find methods for intensifying industrial electrochemical processes. All equations derived for the limiting cathodic current density indicate that its magnitude increases with concentration of reducing particles, c^0, with increasing diffusion coefficient Δ and with decreasing diffusion-layer thickness δ. In order to intensify the cathodic process it is therefore expedient to use solutions with

the highest possible concentration of reducing particles. The optimum concentration is determined in this case by the fact that the solution in the vicinity of the anode (in electrorefining of metals and application of various galvanic coatings) becomes saturated the sooner (i.e., at a lower anodic current density), the higher is the solution concentration. Another way of intensifying an electrochemical process is to raise the electrolyte temperature and thus increase the diffusion coefficient Δ. A third possibility consists in increasing the flow rate or the rate of stirring of the electrolyte, which reduces the diffusion-layer thickness δ[1]. Today this aim is successfully achieved in electrochemical practice by using ultrasound, the imposition of which increases the limiting current density by scores of times. Interesting electrochemical laboratory setups with forced circulation, making it possible to increase the limiting current density to any desired degree, have recently been designed by Gorbachev and coworkers, and also by Gerischer, and others.

The role of diffusion phenomena in electrochemical processes is not, however, restricted to the limitation of their permissible rates. In certain cases, for example, in the electrodeposition of metals, diffusion has an effect on the quality of the deposits formed, in particular, on their distribution over the cathode surface.

Indeed, if, for example, the electrodeposition of a metal is effected in a stationary electrolytic bath with vertical plate electrodes, then, as follows from Eq. (14.42), under the electrolysis conditions chosen the diffusion-layer thickness will increase with distance from the lower edge of the electrode. Under diffusion-controlled conditions (near the limiting current density) more metal will be deposited on the lower than on the higher part of the electrode, i.e., the deposit will be nonuniform and its thickness will decrease from bottom to top. In the case of mixed control, i.e., when the rate of some other step is comparable with that of the transport step or is retarded, the concentration gradient

$$\frac{c_0 - c_{c(h)}}{\delta_h}$$

must reduce to zero with height. Since δ_h increases with increasing h, the value of $c_{c(h)}$ must decrease with h when the gradient is nearly constant. Hence, the concentration of discharging ions will be higher at the bottom than at the top. Such a distribution of concentrations will assist in speeding up any other reaction step at the lower part of the electrode, i.e., the deposit will again be distributed nonuniformly.

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[1] In all cases the optimal parameters must be chosen with account taken of economic factors.

14.2. CHEMICAL (REACTION) OVERPOTENTIAL

14.2.1. THE ROLE OF CHEMICAL STEPS IN THE KINETICS OF ELECTROCHEMICAL REACTIONS

Almost any electrode process involves, as an integral part, a purely chemical transformation. This chemical transformation may be either homogeneous or heterogeneous, it may precede or follow the electrochemical act, but in either case its rate constant does not depend on the electrode potential (since the transformation is purely chemical in nature). Nevertheless this transformation has a noticeable effect on the kinetics of an electrochemical process.

The importance of the chemical step in electrochemical kinetics was first ascertained in the course of polarographic investigations. The fundamentals of the theory of polarographic waves with account taken of diffusion and chemical limitations were elaborated by the Czech school of polarographists: Brdička (1943), and Wiesner and others, and also by Delahay and his coworkers. Later the conceptions of the important role of chemical transformations were extended to other sections of electrochemical kinetics. Thus, Vetter and Gerischer (1951) introduced the concept of reaction overpotential corresponding to the case where the rate of the electrode process is controlled by the conditions under which chemical reactions proceed. In accordance with the classification adopted in this book this type of overpotential is called the *chemical* or *reaction overpotential.*

The physical meaning assigned to the concept of chemical overpotential can be understood by assuming that the overall electrode reaction

$$\nu_A A + \nu_B B + \ldots \overset{zF}{=} \nu_L L + \nu_M M + \ldots \tag{14.51}$$

to which there corresponds the reversible potential

$$\varepsilon_r = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_A^{\nu_A} a_B^{\nu_B} \ldots}{a_L^{\nu_L} a_M^{\nu_M} \ldots} \tag{14.52}$$

involves certain chemical steps. The first chemical step leads to the formation of intermediate particles A′ resulting from the chemical interaction between particles A and B:

$$\nu_A A + \nu_B B = \nu_{A'} A' \tag{14.53}$$

While particles A and B are incapable of electrochemical reduction, particles A′ can be reduced to form new intermediate particles L′:

$$\nu_{A'} A' + z'F = \nu_{L'} L' \tag{14.54}$$

Further transformation of particles L′ gives rise to the final reaction products:

$$\nu_{L'}L' = \nu_L L + \nu_M M \tag{14.55}$$

Reactions (14.53) and (14.55) correspond to chemical transformations, one of which precedes and the other follows the discharging act. Since it is intermediate particles A′ that are discharged and the final products are formed only from intermediate particles L′, the kinetics of each of these two reactions must influence the kinetics of the entire electrode process. If one assumes that all the steps, except the one corresponding to chemical reaction (14.53), proceed unhindered (or are retarded very slightly), the electrode polarization will depend on the activity of particles A′. The activity of these particles can be introduced into Eq. (14.53), making use of the equilibrium constant K_r of reaction (14.53) and putting, for simplicity, $z' = z$:

$$\varepsilon_r = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_{A'}^{\nu_{A'}}}{K_r a_L^{\nu_L} a_M^{\nu_M}} \tag{14.56}$$

If the assumptions made earlier are retained, the activity of particles A′ during the passage of a current must be different and depend on the current density. If the current-induced departure from the equilibrium state is not very great, then the corresponding new value of potential may be expressed by the same equation (14.56) provided the activity $a_{A'(i)}$ of particles A′ at a current density i is substituted for $a_{A'}$:

$$\varepsilon_i = \varepsilon_r' = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_{A'(i)}^{\nu_{A'}}}{K_r a_L^{\nu_L} a_M^{\nu_M}} \tag{14.57}$$

By definition, any value of polarization

$$\eta = \varepsilon_i - \varepsilon_r$$

from which, after substitution of ε_i and ε_r from Eqs. (14.56) and (14.57), one can obtain the following equation for the chemical overpotential η_{ch} due to the slow rate of the chemical step preceding the charge-transfer reaction:

$$\eta_{ch} = \nu_A \frac{RT}{zF} \ln \frac{a_{A'(i)}}{a_{A'}} \tag{14.58}$$

If the rate of the electrode process is governed by the rate of reaction (14.55), then, in place of (14.58), one should write

$$\eta_{ch} = -\nu_{L'} \frac{RT}{zF} \ln \frac{a_{L'(i)}}{a_{L'}} \tag{14.59}$$

Equation (14.59) corresponds to the chemical overpotential caused by the slow rate of the chemical step following the discharge act.

14.2.2. FUNDAMENTALS OF THE THEORY OF CHEMICAL (REACTION) OVERPOTENTIAL

Equations (14.58) and (14.59) are similar in appearance to Eq. (14.6) which was derived earlier under the assumption of retarded diffusion. In both cases a decrease in the concentration of particles being reduced sharply increases polarization ($\eta \to -\infty$) and limits the rise of the current density ($i \to i_l$). But the nature of the processes underlying Eqs. (14.58) and (14.59), on the one hand, and Eq. (14.6), on the other, is essentially different. Under the conditions of diffusion limitations the number of discharged particles is compensated for by particles transported from the bulk of the solution under the effect of the concentration gradient inside the diffusion layer δ. The limiting diffusion current density ${}_di_l$ corresponds in this case to the maximum possible concentration gradient and is a function of the diffusion coefficients of the reacting particles. Conversely, when the purely chemical transformation is retarded, the drop in concentration because of particle discharge is compensated for by the chemical reaction taking place in the immediate vicinity of the electrode or at its surface. The reaction limiting current density ${}_ri_l$ must be a function of the rate constants of the corresponding chemical transformations. The determination of ${}_ri_l$ and the understanding of the laws governing chemical overpotential allows one to study the kinetics of fast chemical reactions by using electrochemical methods.

An idea of the quantitative expression of the reaction limiting current density under stationary conditions can be obtained by considering a rather simplified example of the reactions discussed in the preceding section. Suppose that all the stoichiometric numbers of reactions (14.51), (14.53) and (14.54) are equal to unity and that the amount of substance B greatly exceeds that of substance A, i.e., reaction (14.53) may be regarded as pseudomolecular. Then, if the changes in the composition due to the slow occurrence of reaction (14.53) are localized inside the volume δ_r, the *reaction layer*, the rate of increase of the number and concentration of intermediate particles near the electrode surface ($x = 0$) will be determined by the equation:

$$\left(\frac{dn_{A'}}{dt}\right)_{x=0} = \delta_r \left(\frac{dc_{A'}}{dt}\right)_{x=0} = \delta_r (\vec{k}c_A - \overleftarrow{k}c_{A'})_{x=0} \qquad (14.60)$$

where $\vec{k}$ and $\overleftarrow{k}$ are the rate constants of reaction (14.53) in the forward and reverse directions, respectively. In terms of current

$$i_r = zF\delta_r (\vec{k}c_A - \overleftarrow{k}c_{A'})_{x=0} \qquad (14.61)$$

The maximum rate of formation of particles A′ and, accordingly, the *reaction limiting current* ${}_ri_l$ are attained when $c_{A'} = 0$:

$${}_ri_l = zF\delta_r\vec{k}c_A \qquad (14.62)$$

It should however be taken into account that the same magnitude of current (under stationary conditions) must correspond to the rate of transport of particles A and A′ from the bulk of the solution (if the reaction producing these particles is homogeneous), i.e.,

$$i_d = \text{const}\,[c_A^0 + c_A^0 - (c_A + c_{A'})_{x=0}]$$

or, in the limit, when $c_{A'(x=0)} = 0$

$$_di_l = \text{const}\,(c^0 - c_{A(x=0)}) = i_l \qquad (14.63)$$

where c^0 stands for the sum $c_A^0 + c_{A'}^0$, and i_l corresponds to the limiting current density. Eliminating $c_{A(x=0)}$ from Eqs. (14.62) and (14.63) and solving these equations simultaneously for i_l, one obtains

$$i_l = \frac{zFc^0\delta_r\vec{k}}{1 + \dfrac{zF\delta_r\vec{k}}{\text{const}}}$$

According to Eq. (14.26), under stationary conditions at $t_j = 0$

$$\text{const} = zF\Delta\frac{1}{\delta}$$

and, consequently,

$$i_l = \frac{zFc^0\delta_r\vec{k}}{1 + \dfrac{\delta_r\delta\vec{k}}{\Delta}} \qquad (14.64)$$

If $\delta_r\vec{k}$ is so large ($\delta_r\delta\vec{k} \gg \Delta$) that the unity in the denominator may be neglected as compared with the second term, then

$$i_l = {}_di_l = zF\Delta\frac{c^0}{\delta}$$

i.e., Eq. (14.64) is reduced to Eq. (14.26), which corresponds to purely diffusion limitations.

If, conversely, $\delta_r\vec{k}$ is so small ($\delta_r\delta\vec{k} \ll \Delta$) that the second term in the denominator may be ignored as compared with unity, Eq. (14.64) then simplifies to

$$i_l = {}_ri_l = zF\delta_r\vec{k}c^0 \qquad (14.65)$$

which corresponds to a purely chemical limitation of the rate of the process.

The thickness of the reaction layer, δ_r, can be represented as a function of the diffusion coefficient and the rate constant of a chemical reaction proceeding in the reverse direction

$$\delta_r = \Delta_A\overleftarrow{k}^{-1/2} \qquad (14.66)$$

and thus, in place of Eq. (14.65), one may write

$$_{r}i_{l} = zF\Delta_{A}\vec{k}\cdot\overleftarrow{k}^{-1/2}c^{0} \qquad (14.67)$$

From Eq. (14.67) it follows[1] that, in contrast to the diffusion limiting current density, the reaction limiting current density must be independent of the rate of agitation. Thus, a study into the effect of agitation of the solution on the kinetics of the electrode reaction enables one to distinguish between the hindrance of transport and the chemical transformation. The nature of a retarded chemical transformation can be elucidated on the basis of data on the influence of the electrode material on the kinetics of the electrode process; the absence of this effect indicates that the chemical reaction is homogeneous, whereas the dependence of the kinetics on the electrode material points to the heterogeneity of the chemical transformation.

14.2.3. SOME EXAMPLES OF THE EFFECT OF CHEMICAL TRANSFORMATIONS ON ELECTRODE KINETICS

One of the simplest examples illustrating the role of homogeneous chemical transformations in electrochemical processes is the electroreduction of formaldehyde, which has been thoroughly studied by Brdička and a number of other investigators. In aqueous solutions formic aldehyde is present in a hydrated state and cannot be reduced. For the cathodic reaction to proceed formaldehyde must be preliminarily dehydrated:

$$CH_2O\cdot H_2O = CH_2O + H_2O$$

The free formaldehyde is then converted at the cathode into methanol:

$$CH_2O + 2e^- + 2H^+ = CH_3OH$$

Since the chemical step of dehydration is the most hindered one, a reaction limiting current appears, whose magnitude is governed by the rate constants of the hydration and dehydration reactions:

$$_{r}i_{l} = zF\vec{k}_{dh}\cdot\overleftarrow{k}_{h}^{-1/2}\Delta_{CH_2O\cdot H_2O}(c_{CH_2O\cdot H_2O} + c_{CH_2O})$$

A more complex and still obscure process of electrochemical reduction coupled with the slow stage of homogeneous chemical transformation is the cathodic production of nitric acid from nitrous acid.

[1] The same conclusion can be drawn on the basis of Eq. (14.65) if one takes into account that $\delta_r \ll \delta$ and the reaction layer does not therefore undergo a change with increasing rate of agitation.

According to some authors, the reaction

$$H^+ + NO_3^- + 2H^+ + 2e = HNO_2 + H_2O \qquad (14.68)$$

involves the following steps:

I. $H^+ + NO_3^- = HNO_3$
II. $HNO_3 + HNO_2 = N_2O_4 + H_2O$
III. $N_2O_4 = 2NO_2$
IV. $2NO_2 + 2e = 2NO_2^-$
V. $2NO_2^- + 2H^+ = 2HNO_2$

It is not the initial nitric acid or its ions but the intermediate product, nitrogen dioxide, that is reduced. The reaction leading to the formation of nitrogen dioxide is the sum of steps I, II and III:

$$H^+ + NO_3^- + HNO_2 = 2NO_2 + H_2O$$

with the equilibrium constant

$$K_{NO_2} = \frac{[H^+][NO_3^-][HNO_2]}{[NO_2]^2[H_2O]}$$

Introducing into the equation for the reaction equilibrium potential (14.56)

$$\varepsilon_r = \varepsilon^0 + \frac{RT}{2F} \ln \frac{[H^+]^3[NO_3^-]}{[HNO_2][H_2O]}$$

the concentration of the intermediate product NO_2 yields

$$\varepsilon_r = \varepsilon'^0 + \frac{RT}{F} \ln \frac{[H^+]}{[HNO_2]} + \frac{RT}{F} \ln [NO_2] \qquad (14.69)$$

where ε'^0 includes the quantity K_{NO_2}.

If the formation of NO_2 proceeds at a finite rate, then, owing to the passage of a current, its concentration decreases and becomes equal to $[NO_2]_i$. Since neither the pH value nor the concentration $[HNO_2]$ undergoes a change, one can write, in place of Eq. (14.69):

$$\varepsilon_i = \varepsilon'_r = \varepsilon'^0 + \frac{RT}{F} \ln \frac{[H^+]}{[HNO_2]} + \frac{RT}{F} \ln [NO_2]_i \qquad (14.70)$$

The reaction overpotential

$$\eta_r = \varepsilon_i - \varepsilon_r = \varepsilon'_r - \varepsilon_r = \frac{RT}{F} \ln \frac{[NO_2]_i}{[NO_2]} \qquad (14.71)$$

arising in this case at the step preceding the discharging act will be determined by the kinetics of homogeneous chemical reactions producing nitrogen dioxide.

The indicated scheme however contradicts the fact of the appearance of NO in the reaction volume. Another scheme has therefore

been suggested, according to which reaction (14.66) involves the following three basic steps:

$$\text{I. } 2HNO_2 + 2H^+ = 2NO^+ + 2H_2O$$
$$\text{II. } 2NO^+ + 2e = 2NO$$
$$\text{III. } HNO_3 + 2NO + H_2O = 3HNO_3$$

Here step III following the charge-transfer reaction is considered to be the slow one. Although no unequivocal conclusion can be made as to which of the two schemes indicated is preferable, it should nevertheless be noted that in both cases the kinetics of the electrode process is controlled by purely chemical homogeneous transformation.

Numerous examples of electrochemical processes in which the homogeneous chemical reaction plays an important role have been obtained in polarographic investigations of the reduction of the various inorganic and organic substances, in particular organic acids. It has been found that undissociated molecules of acids are reduced more readily than their anions. In solutions of high pH value, however, even weak acids are present mainly in the ionized state. Therefore, in a definite region of pH values dependent on the dissociation constant of the acid two waves appear on polarograms, one corresponding to the reduction of the molecules, and the other to that of acid anions. The measured limiting current of the first wave is found to be considerably higher than expected in the case of diffusion limitations. Here the loss of acid molecules is compensated for not only by diffusion, but by another, more effective process. This second process is identified with the formation of undissociated molecules of the acid from its anions and hydrogen ions. The rate of this reaction depends on the rate constants of recombination k_{rec} and dissociation k_{dis} and also on the solution composition:

$$\frac{d[HA]}{dt} = k_{rec}[H^+][A^-] - k_{dis}[HA] \qquad (14.72)$$

The height of the second wave is governed by the concentration of acid anions near the electrode. A study of the dependence of the wave height on the solution pH and a comparison of these values with diffusion limiting currents allows one to obtain data required for calculating the rate constants of the chemical reactions preceding the discharge step. Thus, the reduction of pyroracemic acid to lactic acid

$$CH_3COCOOH + 2H^+ + 2e = CH_3CHOHCOOH$$

yielded the following data. At pH < 4 only one wave of height h is detected on the polarogram. Since the dissociation constant of pyroracemic acid is 3.2×10^{-3} mole/litre, it follows that at such pH values practically only undissociated molecules of the acid are

present in solution. If pH > 4, two waves appear instead of one, their total height remaining practically unaltered and independent of pH. At a pH value of about 6.1 the height of each wave is approximately half of h and, finally, at pH > 7.6 again only one wave is left on the polarogram. It starts at a more negative potential than the vanished first wave and corresponds to the reduction of the acid anions. Polarograms obtained over a wide range of pH values have enabled calculation of the k_{rec} and k_{dis} of pyroracemic acid; they are equal to 7.08×10^8 mole^{-1}/litre·sec^{-1} and 2.24×10^6 sec^{-1}, respectively.

The course of electrochemical processes is affected almost as often by heterogeneous chemical transformation. A typical example is the cathodic evolution of hydrogen, in which the final product (hydrogen molecules) is obtained through recombination of the adsorbed hydrogen atoms resulting from the discharge act:

$$2H_{ads} = H_2$$

If the recombination reaction proceeds slowly, it gives rise to polarization. The magnitude of polarization can be determined by inserting the activity of atomic hydrogen in Eq. (14.61):

$$\eta_{ch} = -\frac{RT}{F} \ln \frac{a_{H(i)}}{a_H} \qquad (14.73)$$

The anodic evolution of oxygen should also be included in this group of processes if its rate is determined, for example, by the steps of formation (or decomposition) of higher oxides of the electrode metal.

An example of the accelerating effect of chemical reactions is the increase of the limiting current during the reduction of ferric ions to ferrous ions upon addition of hydrogen peroxide to a solution of an iron salt. The polarographic reduction of trivalent ferric ions occurs at potentials at which hydrogen peroxide is not reduced at the mercury cathode. The observed increase of the limiting current cannot therefore be ascribed to the superposition of the wave of reduction of hydrogen peroxide upon that of ferric ions. This fact can however be explained if it is assumed that the ferric ions (formed at the cathode surface as a result of discharge) are chemically oxidized by hydrogen peroxide with recovery of iron ions of higher valency:

$$Fe^{3+} + e = Fe^{2+} \qquad (14.74)$$

$$Fe^{2+} + \frac{1}{2} H_2O_2 = Fe^{3+} + OH^- \qquad (14.75)$$

which subsequently participate in the reduction reaction. The decrease in the concentration of ferric ions is compensated in this case not only by diffusion but also by a chemical reaction. The rate constant of this reaction, described by Eq. (14.75), can be calculated by comparing the actual wave heights with the values of diffusion limiting current. The value of the rate constant thus obtained agrees fairly well with the value found by another method.

CHAPTER 15

Phase Overpotential

15.1. GENERAL DESCRIPTION OF PHASE OVERPOTENTIALS

The term *phase overpotential* suggested by Gorbachev gives a true reflection of the nature of the phenomenon. The deviation of the electrode potential from the equilibrium value during the passage of a current is caused by difficulties associated with the formation and development of a new phase under the conditions of electrolysis. It is therefore appropriate to recall here certain general points concerning phase transformations.

All phase transformations can be divided into two groups according to the character of transition from one phase to another. Phase transformations of the first group are not accompanied by metastability phenomena, i.e., superheating, supercooling or supersaturation. To this group belong transformations of a solid phase S into a liquid L or gas phase V, i.e.,

$$S \rightarrow L$$

and

$$S \rightarrow V$$

Phase transformations $S \rightarrow L$ (melting) and $S \rightarrow V$ (sublimation) occur at the surface of a solid and are not associated with an increase in the surface area of the interface and hence with an increase in the free energy. A solid cannot be superheated to a temperature above its melting or sublimation point.

The second group includes the following phase transformations characterized by metastability phenomena:

1. $S_1 \rightarrow S_2$ = formation of a new solid compound, or recrystallization.
2. $L \rightarrow S$ = formation of a precipitate, or crystallization from a melt.
3. $V \rightarrow S$ = transition from gas to solid, which is also called sublimation.
4. $L \rightarrow V$ = boiling.
5. $V \rightarrow L$ = condensation.

In all these transitions the formation of a new phase involves nucleation and is invariably associated with an increase in the surface area of the interface and hence with an increase in the free energy of the system. By a three-dimensional nucleus is understood

the microformation of a new phase with dimensions ensuring the attainment of equilibrium with the surrounding medium, i.e., the phase inside which it originated. In transformations $S_1 \rightarrow S_2$, $L \rightarrow S$ and $V \rightarrow S$ this is a nucleus of a solid phase originating from the corresponding changes of the solid S (recrystallization, formation of a new solid chemical substance), liquid L (crystallization, precipitation) or gas V (sublimation) phase. In transformations $L \rightarrow V$ and $V \rightarrow L$ this will be nuclei of vapour (gas bubbles formed upon boiling) or liquid (drops formed upon condensation). In all these cases the transition from one homogeneous phase to the other proceeds via an intermediate state corresponding to a microheterogeneous system, in which the nuclei of a new phase are distributed inside the original one. This intermediate, or transition, state is characterized by an increased amount of energy owing to the presence of numerous interfaces and its formation requires an activation energy determined by the energy of formation of three-dimensional nuclei.

What has just been said can be illustrated by the process of condensation, i.e., the phase change $V \rightarrow L$. Under definite conditions, i.e., at a definite vapour pressure P and temperature T, the appearance of three-dimensional nuclei of a new phase (liquid drops) in the vapour phase becomes possible. From the surface of these drops the molecules of the substance can be converted into the vapour phase. Since the volume of a body decreases proportionally to the cube and its surface proportionally to the square of linear dimensions, it follows that with decreasing linear dimensions the relative fraction of molecules residing on the surface must increase and their transition into the initial phase becomes more probable. It is therefore obvious that to suppress the process of evaporation and preserve the liquid nucleus it is necessary to increase the vapour pressure; the smaller is the size of the drops the higher must be the vapour pressure. In other words, the equilibrium vapour pressure above the drop is a function of its size, which can be expressed mathematically by the Thomson formula:

$$RT \ln \frac{P_{r_1}}{P_{r_2}} = \sigma \frac{M}{d} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \tag{15.1}$$

where P_{r_1} and P_{r_2} = equilibrium vapour pressure above drops of radii r_1 and r_2 ($r_1 < r_2$)
σ = interfacial tension
M = molecular weight of the substance whose phase transformation is considered
d = density of this substance in the liquid state.

For a phase of finite dimensions $r = \infty$ and the Thomson formula takes the form

$$RT \ln \frac{P_{r_1}}{P_\infty} = \sigma \frac{M}{dr} = \sigma \frac{V}{r} \tag{15.2}$$

where r = radius of the drop

V = molar volume of the substance in the liquid state.

From Eq. (15.2) it follows that $P_r > P_\infty$, i.e., the vapour pressure above a drop of radius r is always greater than above the liquid itself. The quantity $RT \ln (P_r/P_\infty)$ may serve as a measure of supersaturation required for the formation of nuclei of radius r: it will be the greater the higher is the interfacial tension σ (the excess

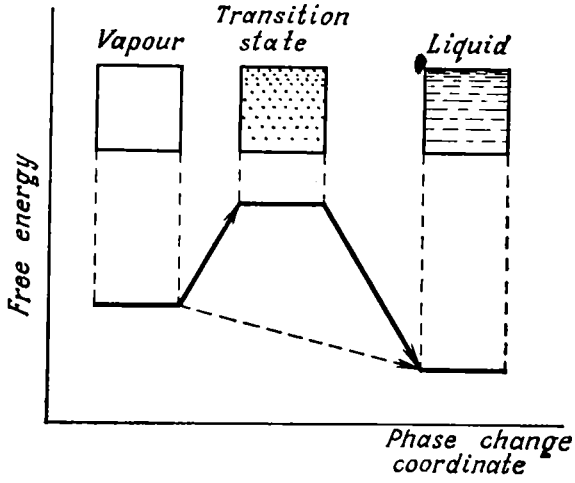

Fig. 15.1. Two types of phase transformations

surface energy) and the smaller the radius of the drop, r. The transition from the vapour to the liquid state is shown schematically in the diagram of Fig. 15.1 pertaining to conditions when the liquid is the more stable (its free-energy level is lower than that of vapour). The same reasoning is valid for the formation of nuclei of a solid or vapour phase.

The formation of nuclei of size r requires an energy U_3, which can be estimated for the case of liquid drops by the equation

$$U_3 = \frac{16\pi\sigma^3 \left(\frac{M}{d}\right)^2}{3\left(RT \ln \frac{P_r}{P_\infty}\right)^2} \qquad (15.3)$$

Similar relationships hold for nuclei of other phases.

15.2. PHASE TRANSFORMATIONS IN ELECTROCHEMICAL PROCESSES

15.2.1. FORMATION OF A NEW PHASE

Electrochemical processes very often involve the formation of a new phase. For example, the electrolysis of alkali solutions gives rise to gas phases (hydrogen and oxygen) resulting from the decom-

position of a liquid phase (water), and the electrolysis of chloride solutions leads to the evolution of gaseous hydrogen and chlorine. When solutions of metal salts are subjected to electrolysis, new liquid (Hg, Ga) or solid (Cu, Zn, Pb, Ni, Cd, etc.) metallic phases are formed at the cathode. When an acid accumulator is being charged, solid lead sulphate is transformed to metallic lead at one of the electrodes and to lead dioxide at the other. The number of such examples could be considerably increased, but what has been said is sufficient to illustrate how often one has to reckon with the formation of new phases in the course of electrochemical processes.

When a new phase is formed electrolytically, its energy level, in contrast to ordinary phase transformations, is not necessarily lower than that of the initial phase and the process may proceed with increase in the free energy of the system, this energy being supplied in the form of electrical power. The direction of a phase change is determined in this case by the magnitude and sign of the electrode potential rather than by temperature and pressure.

If the slow step of an electrochemical process is the formation of a new phase and all other steps proceed at a faster rate and may be considered reversible, then

$$\varepsilon_i - \varepsilon_r = \eta_{ph} \tag{15.4}$$

where η_{ph} is the *phase overpotential*. The probability of three-dimensional nucleation is determined by the quantity U_3 and consequently its rate under the conditions of an electrochemical process, i.e., the current density i, must also be a function of U_3:

$$i = ke^{-U_3/RT} \tag{15.5}$$

On the other hand, the magnitude of phase overpotential must be proportional to the supersaturation of the system and

$$zF\eta = RT \ln \frac{P_r}{P_\infty} \tag{15.6}$$

Substitution of the value of U_3 from Eq. (15.3) into Eq. (15.5) and replacement of $RT \ln (P_r/P_\infty)$ by $zF\eta$ gives

$$i = ke^{-\frac{16\pi\sigma^3\left(\frac{M}{d}\right)^2}{3(zF\eta_{ph})^2} \cdot \frac{1}{RT}} \tag{15.7}$$

or

$$\ln i = \ln k - \frac{16\pi\sigma^3\left(\frac{M}{d}\right)^2}{3z^2F^2} \cdot \frac{1}{\eta_{ph}^2} \cdot \frac{1}{RT} \tag{15.8}$$

This relationship has not yet been observed experimentally for the evolution of gaseous products. Evidently, the formation of a gas phase is hindered lessthan the other steps—diffusion, charge-trans-

fer, and chemical transformations. However, it has been confirmed quantitatively for the deposition of Ag, Hg and Pb at a cathode made of a single crystal of Pt. For example, the experiments carried

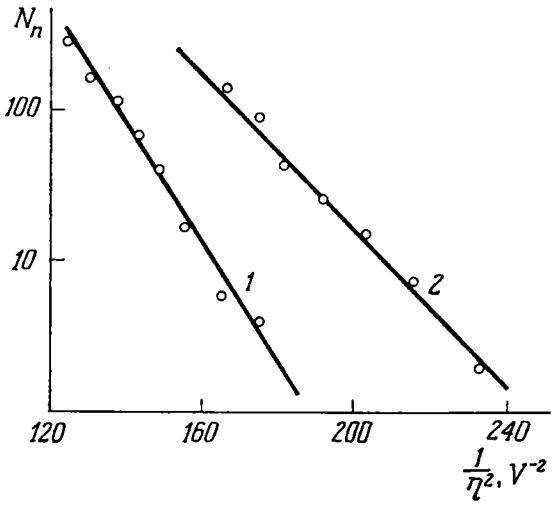

Fig. 15.2. Dependence of the number of three-dimensional nuclei on the inverse square of overpotential for cathodic deposition of mercury on the platinum electrode:

1—on the (001) face; *2*—on the (111) face

out by Kaischew and Mutafchiew (Bulgaria) have shown that the number of mercury nuclei formed after the passage of a short-time current pulse is linearly dependent on the inverse square of the overpotential (see Fig. 15.2).

15.2.2. THE GROWTH OF A CRYSTALLINE PHASE

In the experiments mentioned above the surface of platinum was covered, on prolonged electrolysis, with the corresponding metal, whose further deposition is attended by crystallization, or crystal growth alone, without the formation of a new phase. The hindered growth of a solid crystalline phase may also be responsible for the buildup of a phase overpotential, which should be called the *crystallization overpotential* η_{cr} in this particular case. The crystallization overpotential has been studied most thoroughly in the case of electrodeposition of metals, although there are works devoted to the formation of oxide and other films on the anode surface. In order to understand the essence of the crystallization overpotential it is necessary first to have a look at metals from the viewpoint of morphology.

Solid metals are crystalline bodies, i.e., are built up of identical unit cells, in the lattice points of which partly ionized atoms are situated. A repetition of such identical unit cells in space forms

a crystal of finite size homogeneous and anisotropic in different directions. Most metals crystallize in one of the following three lattice structures: cubic body-centred (e.g. alkali metals, Ba, α-Fe, Mo, W) which is the α-iron structure; cubic face-centred (Ca, Sr, Ni, Al, Ti, γ-Fe, β-Co, Cu, Pt) which is the copper structure; and hexagonal (Be, Mg, α-Co, Ti, Os) which is the magnesium structure.

The primitive cell of the cubic body-centred structure is a cube with atoms (or ions) of a corresponding metal located at its corners and in its centre. The basic unit of the cubic face-centred structure is a unit cell corresponding to a cube, in which structural units (atoms or ions) are situated at the corners and in the centre of each face. The hexagonal lattice structure is built up of hexagonal prisms with the corresponding structural units located at the corners. Since all crystals are built up of identical unit cells that repeat themselves indefinitely in three dimensions, they are characterized by symmetry, i.e., the coincidence of identical parts of figures in symmetry operations (rotation, reflection, etc.).

The basic elements with respect to which symmetry operations are carried out are the centre of symmetry, the axis of symmetry and the plane of symmetry. In the case of the cubic lattice structure three mutually intersecting edges of a cube may be chosen as the axes of symmetry. For the hexagonal structure the 4-fold axis of symmetry is usually used.

Each possible face of a crystal can be determined from the intercepts which it cuts on the axes of reference. Most often use is made of the ratio (known as the *axial ratio*) of the intercepts of the unit face on the axes of reference to the intercepts of a given face on the same axes. These axial ratios are whole numbers and a set of these ratios constitutes the symbol of a face: (h, k, l) for cubic lattices and (h, k, l, m) for hexagonal lattices; each of the quantities enclosed in parentheses is an index of a crystal face. It is customary to choose, as a unit or reference face, a face which intersects all three axes of reference. Faces characterized by a set of identical indices written in different sequences, such as (100) or (010), are also identical. Different faces are designated by sets of different indices. For example (100) is the face of a cube, (110) the face of a prism, and (111) the face of an octahedron. Faces having different symbols differ also in packing density, i.e., the number of atoms per unit surface area (usually per 1 cm^2). For example, the ratio of packing density for three faces in the face-centred lattice (the copper structure) is $N(011) : N(001) : N(111) = 1 : 1.38 : 1.63$, or in absolute value:

Face	Packing density (number of atoms per 1 cm^2)
(011)	$4.02 \times 10^{15} \times V_A^{-2/3}$
(001)	$5.56 \times 10^{15} \times V_A^{-2/3}$
(111)	$6.57 \times 10^{15} \times V_A^{-2/3}$

where V_A is the atomic volume. Since V_A is different for different substances, the packing density must be a function not only of the face symbol but also of the nature of the substance. As the packing density for these faces is different, it follows that many other properties, such as the rate of growth (exchange currents), the surface potential and hence the electronic work function, and the null point, must also be different, which should be taken into account in treating processes of electrocrystallization.

An electrolytic metallic deposit can thus be described by its crystallographic structure. For instance, the crystallographic structure of electrolytically deposited copper will always correspond to the structure of the face-centred cubic lattice. Depending on the electrolysis conditions, one can obtain deposits having two or three different crystallographic structures for some metals (e.g. iron, manganese).

All these specific features of the structure of crystalline bodies must be taken into account when considering the processes of nucleation and crystal growth during electrolysis, in particular, during the cathodic deposition of metals. The similarity between the electrolytic deposition of metals and the formation of crystals from the gas, liquid or solid phase is reflected in the term *electrocrystallization* coined by Kistyakovsky.

A crystal in equilibrium with the environment assumes a shape corresponding to its minimum surface energy:

$$\Sigma \sigma_i \Omega_i = m_i n \tag{15.9}$$

where σ_i and Ω_i are the surface tension and the surface area of an ith face, respectively. Wulff (1901) proposed the following method for finding out the shape of an equilibrium crystal. From any point in space draw, in the directions of possible crystal faces (Fig. 15.3), vectors whose lengths h_i are proportional to the surface tensions σ_i of the faces perpendicular to them. The smallest part of the space, which is bounded by planes passing through the vector end points and contains the origin, will be the equilibrium shape of the crystal satisfying Eq. (15.9). For an equilibrium crystal

$$\frac{\sigma_i}{h_i} = \text{const} \tag{15.10}$$

For the formation of nuclei of a solid phase this quantity should be substituted into the Thomson equation for the ratio σ/r.

The growth of each face of a crystal is governed by the conditions under which new structural units (atoms or ions) land on its surface.

During the growth of a crystal formed from a gas phase or melt of a given substance, for example, from a molten metal, the attachment of each new structural unit on the crystal face is the result of its interaction with lattice-atom neighbours.

Since the packing density is different for faces having different indices, their growth rates must also be different. For general treatment of the problem, however, this difference may be ignored, assuming that the most important factor here is the interaction of the new structural unit (an adion) only with underlying metal atoms in direct contact with it.

At the beginning of the growth of a face the attachment of new structural units, say, metal ions, on the face plane (planar site I)

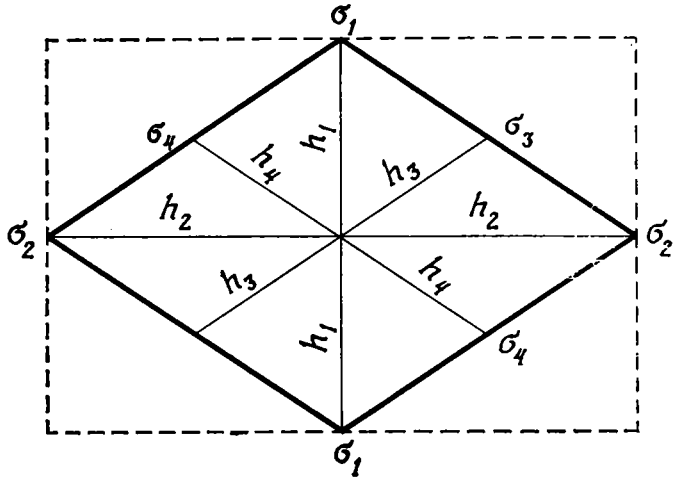

Fig. 15.3. Finding the equilibrium crystal shape according to Wulff (the plane model)

results from interaction with only one lattice-atom neighbour (Fig. 15.4*a*). We will denote this energy of interaction with one neighbour as a.

When a larger number of atoms have landed on the crystal face, they may agglomerate and form monoatomic islands of different shape (Fig. 15.4*b*). The addition of new atoms to the step (step site II) is facilitated by contact with two neighbours and in this case the interaction energy is equal to $2a$.

Further, surface monoatomic layers with kinks may form (Fig. 15.4*c*), in which case the addition of a new atom is facilitated by interaction with three close neighbours (kink site III); here the interaction energy is $3a$. After this surface layer has been formed the addition of each next atom to it is accompanied by an energy gain of $3a$; only at the beginning of the growth of each new row of atoms does the gain of energy equal $2a$, this providing a so-called "repeating step" and the highest rate of spreading of the atomic monolayer over the surface, i.e., the fastest growth of the crystal face. When this monolayer of atoms covers the whole face plane, further growth will proceed via the same steps (a, b and c) until a two-dimensional island is formed, providing a repeating step.

Evidently, the hindrance to the face growth is the least during the formation of such an island, which, by analogy with a three-dimensional nucleus, was named a two-dimensional nucleus. The rate of

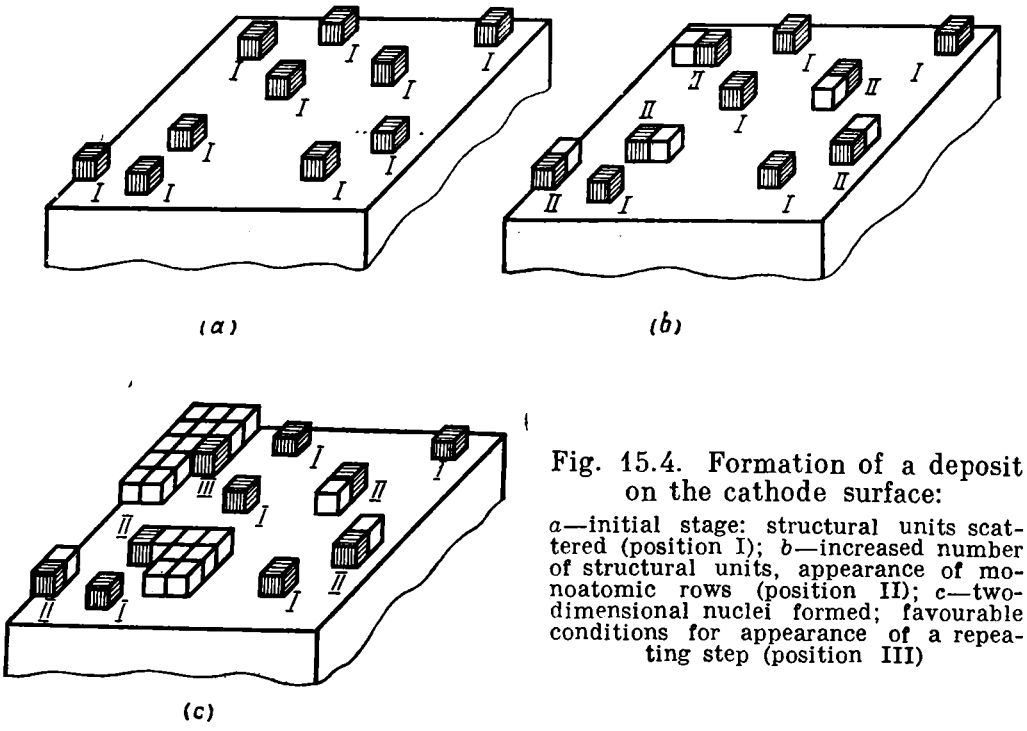

Fig. 15.4. Formation of a deposit on the cathode surface:
a—initial stage: structural units scattered (position I); *b*—increased number of structural units, appearance of monoatomic rows (position II); *c*—two-dimensional nuclei formed; favourable conditions for appearance of a repeating step (position III)

face growth, i.e., the rate of formation of a crystalline phase, must therefore be a function of the energy required to create a two-dimensional nucleus; this energy U_2 is determined from the equation

$$U_2 = \frac{\pi\sigma_d^2\Omega_M}{RT\ln(P_l/P_\infty)} \qquad (15.11)$$

where σ_d = edge stress characterizing the excess free energy at the edges of the nucleus
Ω_M = surface area occupied by one gram-molecule of the substance
P_l = equilibrium vapour pressure above a nucleus of perimeter l
P_∞ = equilibrium vapour pressure above a given solid phase of finite dimensions.

Volmer (1930) assumed that the above mechanism of crystal growth from the vapour phase may be extended to the case of electrocrystallization of metals. The rate of face growth (in terms of current density) can then be expressed by the equation

$$i = ke^{-U_2/RT} \qquad (15.12)$$

Assuming, as before, that the overpotential corresponds to supersaturation

$$zF\eta_{cr} = RT \ln \frac{P_l}{P_\infty} \tag{15.13}$$

Volmer deduced an equation relating the current density to the crystallization overpotential

$$\ln i = \ln k - \frac{\pi\sigma_d^2\Omega_M}{RTzF} \cdot \frac{1}{\eta_{cr}} \tag{15.14}$$

15.2.3. THE CRYSTALLOCHEMICAL THEORY OF ELECTROCRYSTALLIZATION

Until quite recently nobody succeeded in creating such conditions of electrolysis under which the slow step would be the formation of two-dimensional nuclei and the deviation of the electrode potential from the equilibrium value on passage of a current would correspond to the crystallization overpotential:

$$\varepsilon_i = \varepsilon_r = \eta_{cr}$$

Only very recently (1966) Budewski and coworkers demonstrated the possibility of such a process. They conducted experiments with the ideal face (111) of silver serving as the cathode, with the use of the pulse technique. In these experiments a short-time current pulse was imposed on the cathode, which resulted in a shift of the potential sufficient for the formation of a two-dimensional nucleus; then the potential shifted to the positive side, which excluded the possibility of formation of new two-dimensional nuclei but ensured the growth of the existing nucleus. The current flowing through the cell first increased and then, after the advancing crystal front reached the edge of the face, dropped to zero. For the crystal face to keep growing further the potential had to be shifted again to the negative side, to values ensuring the formation of a new two-dimensional nucleus. The results obtained by Budewski have shown that there are periodic oscillations of the current at a pre-set potential or of the potential at a constant current, and that the growth of a crystal face involves the formation of a two-dimensional nucleus and its spreading over the surface. This mechanism however operates only in certain limiting cases which are not realizable because of a number of factors. Some of these factors were taken into account in the crystallochemical theory of electrocrystallization developed by Gorbunova and Dankov; this theory may be regarded as a further development of Volmer's views.

The crystallochemical theory presupposes the possibility of the formation of pile-ups of growth layers (consisting of several "storeys" of two-dimensional nuclei) when the effects of surface passivation and change of the ionic concentration of the solution are superimpo-

sed near the advancing growth front. It is assumed that the part of the surface which has been in contact with the solution for a long time becomes blocked and additional energy is required for a new two-dimensional nucleus to be formed on it. Conversely, the surface of a newly born two-dimensional nucleus remains free of adsorbed extraneous particles and a new two-dimensional nucleus may form on it with a smaller amount of energy consumed. The thickness of such a pile-up is limited by the decrease of the concentration in the zone where two-dimensional nuclei are piled up, and the growing electrodeposit can therefore move only along the face plane rather than normally to it. The existence of pile-ups of two-dimensional nuclei has been observed experimentally by many authors.

15.2.4. THE ROLE OF SURFACE MICROSTRUCTURE AND DEFECTS IN ELECTROCRYSTALLIZATION PROCESSES

The passivation and concentration effects undoubtedly play an important role in the processes of crystal growth, but they are not the only causes responsible for the departure of the actual picture of crystallization from the idealized Volmer model; moreover, they are not always the principal factors. One of the causes should be sought in disturbances of the perfect crystal structure, i.e., in crystal lattice defects, and primarily in the appearance of portions in which the arrangement of structural units is different from that in the perfect lattice of a given crystalline body (so-called *dislocations*).

Figure 15.5 shows a screw dislocation which results in a monomolecular step on the crystal surface. The addition of even the first structural unit to the edge of the dislocation results in an energy gain of $2a$ and ensures the appearance of a repeating step with an energy gain of $3a$. With the addition of new units the dislocation step will advance in the direction *1*. Simultaneously at the dislocation centre *O* a new step appears, which is perpendicular to the initial direction of the dislocation; this step is also capable of further growth but in the direction *2*. At the new centre of dislocation, again, there appear favourable conditions for the formation of a repeating step in the direction *3*, and so after a certain period of time under current the initial dislocation will grow into a spiral front. A crystal surface may have a large number of dislocations, in which case several spiral fronts are formed simultaneously, this resulting in the deposition of a metal at a low crystallization overpotential. These conditions were realized in experiments on electrolytic deposition of silver carried out by Kaischew. Extraneous atoms and molecules that find their way into the deposit disturb the lattice structure and contribute to the formation of dislocations on its surface during electrodeposition. Thus, the appearance of a crystal defect on the face plane promotes the process of crystallization. If the number

of defects (dislocations) per unit surface area is sufficiently large, i.e., at a high density of defects, the need for two-dimensional nucleation is eliminated. A theory of crystallization and electrocrystallization taking into account the role of dislocations has been formulated in the works of a number of researchers (Burton, Cabrera and Frank, Kaischew, Fischer, Lorenz and their coworkers, Vermilyea, and others); this theory is in good agreement with experimental

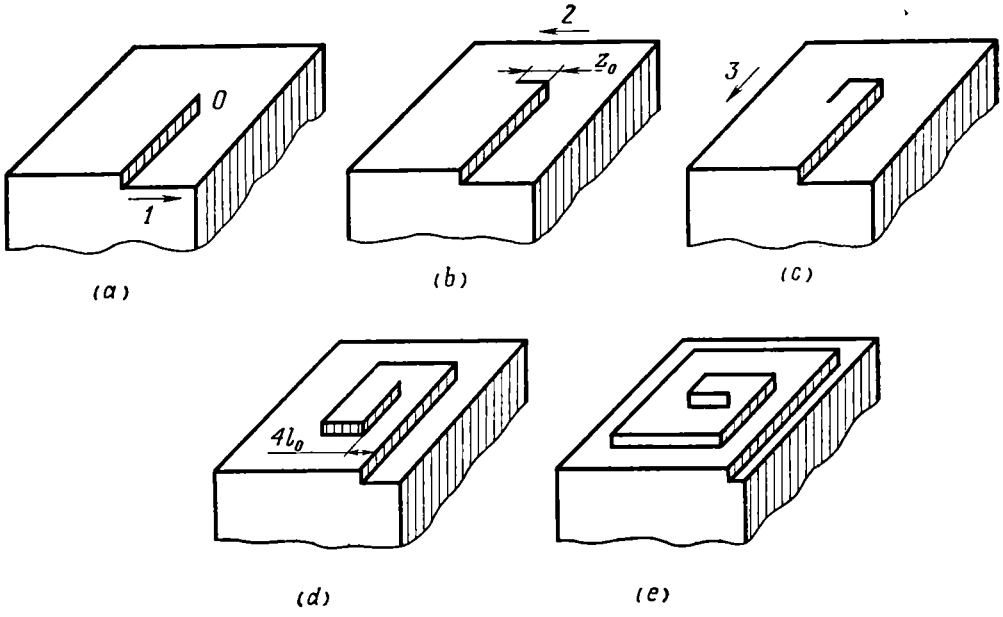

Fig. 15.5. Spiral growth of a crystal caused by a dislocation

evidence. For one thing, it follows from this theory, in conformity with experimental data, that the crystallization overpotential is lower than could be expected on the basis of the Volmer theory, which ascribes the decisive role to two-dimensional nucleation. The new theory also accounts for the spiral growth observed during the electrodeposition of many metals on the surface with screw dislocations and for a number of other experimental facts.

15.2.5. THE ROLE OF DEHYDRATION PHENOMENA IN THE CATHODIC DEPOSITION OF METALS

The departure of the Volmer theory from experiment may also be attributed to the neglect of the difference between crystallization from the vapour phase and electrocrystallization. In the former case the atoms or molecules of a substance are in a free state, and in the latter they are present in solution in the form of ionic or other complexes. In the cathodic deposition of a metal from a solution of its simple salt a metallic ion has to divest itself of its sheath of

hydration water before it can be incorporated into the metal lattice. This process requires considerable energy, of the order of tens or hundreds of kilocalories. Indeed, as follows from Table 3.9, the hydration energies of ions (except univalent ions of large size) exceed, as a rule, 100 kcal/g-ion. Bockris and Conway (1958) pointed out that taking into account dehydration greatly changes the picture of lattice incorporation during electrocrystallization as compared with the Kossel-Stranski model on which the Volmer theory is based. When an ion enters the crystal lattice, it loses completely its hydration sheath and its charge is compensated by the electron gas in the metal. Three variants at least may be visualized here. The first variant is a charge transfer to any site on the cathode with simultaneous complete dehydration of the ion and addition of a metal atom to the electrode surface. In this case the incorporation of the ion into the metal lattice will occur according to a scheme corresponding to the Volmer theory. However, as first noted by Lorenz (1954), the metal atoms formed on the surface differ in their energetic properties from the particles in the metal lattice. Lorenz named such atoms adatoms (adsorbed atoms). Since the advancing crystal front (two-dimensional nuclei, dislocations) occupies only a relatively small fraction of the entire cathode surface, the largest number of adatoms must form on the plane (plane site I) and not on growth sites (step site II and kink site III). To reach the growth step, adatoms have to diffuse along the surface until they find a suitable site (position III or II) to be incorporated into the lattice. The driving force for such surface diffusion is the concentration gradient or, more precisely, the activities of adatoms. Surface diffusion is thus a necessary link in the process of electrocrystallization and may be its rate-determining step, which is not taken into account by the Volmer theory.

The second variant corresponds to the assumption that the loss of the hydration sheath and the charge-transfer step occur only at sites where the energy gain is the greatest owing to coordination with neighbouring metal atoms which are part of the crystal lattice of the cathodic metal deposit. In this case the completely hydrated ion moves through the solution, in the region of the double layer, parallel to the cathode surface until it reaches a site where charge transfer and dehydration are facilitated (i.e., a growth side providing a repeating step of crystallization). No surface diffusion of adatoms occurs in this case and dehydration, charge transfer and lattice incorporation take place as a single act.

The third variant is based on the assumption that dehydration proceeds stepwise and so-called adions, instead of adatoms, participate in the process of electrodeposition. The least distortion of the hydration sheath is observed when the ion lands on the face plane. Suppose, for example, that six water molecules form the primary

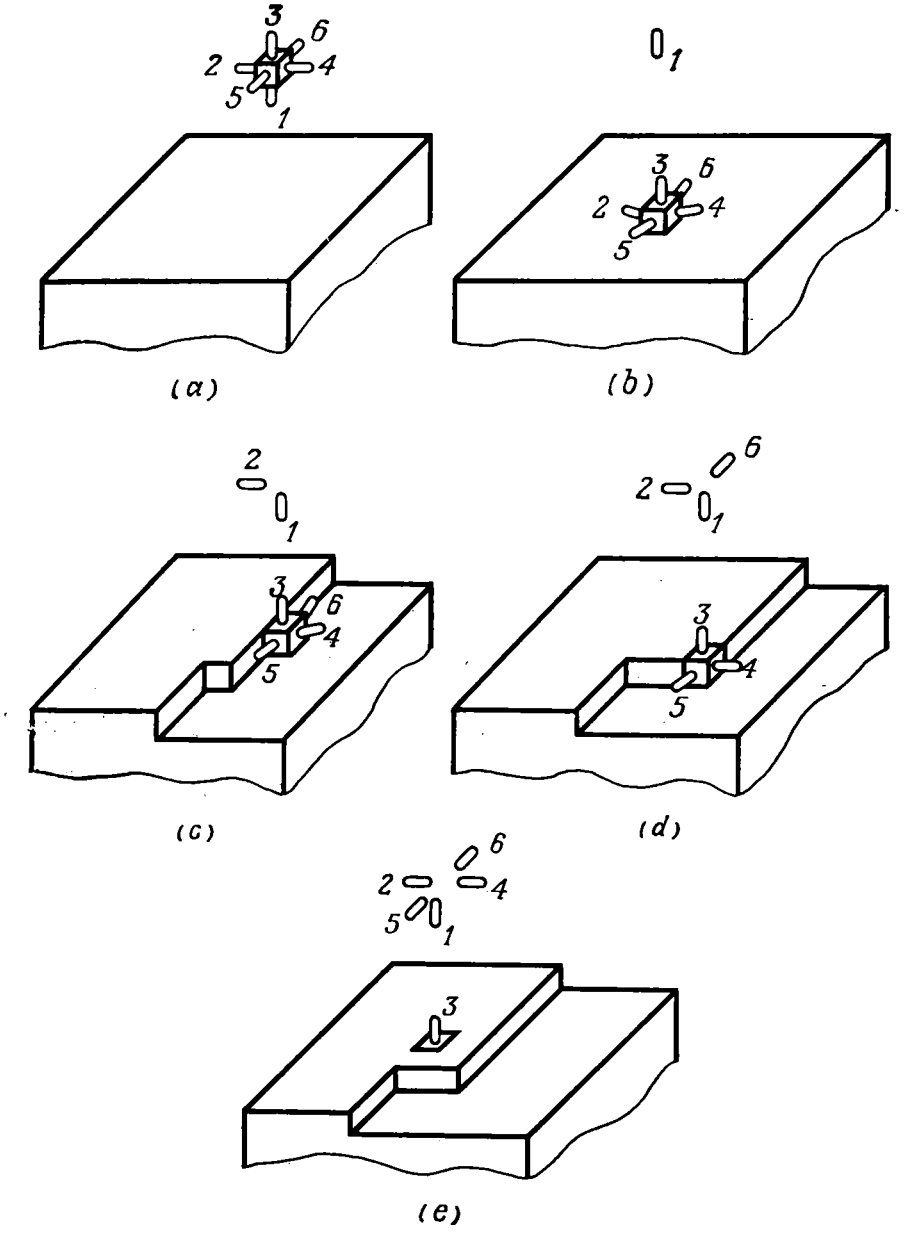

Fig. 15.6. A model illustrating dehydration of an ion at its different positions relative to the cathodic deposit:

a—in solution, $n_h = 6$; *b*—on the face plane; *c*—on the edge of a two-dimensional nucleus; *d*—on the kink; *e*—in the surface layer of the deposit

hydration layer of the ion-water complex (Fig. 15.6); when the ion lands on the crystal face, its hydration sheath is slightly distorted with the resulting loss of one water molecule (Fig. 15.6*b*). The partially dehydrated ion acquires a metal atom neighbour and the electrons in the metal partly neutralize the positive charge of the ion. Such a partially neutralized and partially dehydrated

ion on the metal surface is called an *adion* (adsorbed ion). When the aquated ion lands on the edge of a two-dimensional nucleus (on a step site), the distortion of its hydration sheath is relatively greater because of steric hindrances and the ion loses not one but two water molecules (Fig. 15.6*c*), which requires more activation energy as compared with its landing on the plane. Still more energy is needed when the ion lands on a kink site (Fig. 15.6*d*), where three water molecules are lost and the bond with the metal becomes stronger. The ion is completely dehydrated and gets embedded in the lattice only when it is surrounded from all sides by metal ions, as shown schematically in Fig. 15.6*e*. Thus, if the energy supplied during the coordination of the aquated ion with metal ions does not compensate the energy spent on dehydration of the ion, then, in contrast to the Kossel-Stranski model, the ion will land on the crystal plane rather than on the site of a repeating step. This inference has been drawn from the calculations made by Conway and Bockris for the case of silver deposition at a potential corresponding to the null point. According to their conceptions, the electrodeposition of metals involves the intermediate formation of adions on the crystal plane, surface diffusion to growth sites and incorporation into the metal lattice. As in the Lorenz theory, one of the steps in this case is surface diffusion, the only difference being that adions are involved instead of adatoms.

At present it is difficult to decide which of the mechanisms considered above is the most probable; still, preference should evidently be given to the last two versions. The existence of adatoms and adions has been confirmed independently by a number of workers using different methods, which have also allowed their concentration to be determined. Surface diffusion of particles is most important in those cases when growth sites (dislocations, two-dimensional nuclei) occupy only a small portion of the surface. Then, owing to a large distance x_d which the adsorbed particles must cover before they get incorporated into the metal lattice, the concentration gradient $\Delta c_{ad}/x_d$ and hence the rate of surface diffusion will be low, in which case surface diffusion may become the slow step (rds) in the electrodeposition of metals. These conditions are possible on faces without defects (or faces with a small number of defects) and at low polarizations (small current densities) when the number of nuclei is small. With increasing polarization the number of active centres (growth sites) becomes larger as a result of an increase in the number of two-dimensional nuclei and conversion of inactive growth sites into active (depassivation). Besides, as the potential assumes more negative values, the concentration of particles increases. All this results in an increased concentration gradient, and surface diffusion ceases to be the slow step. The deposition rate will be limited by some other step, usually by the charge-transfer step.

At still higher polarizations the transport of ions to the electrode surface becomes the rate-determining step, and the electrode potential will be governed by the transport overpotential.

15.3. SPECIFIC FEATURES OF THE CATHODIC FORMATION OF POLYCRYSTALLINE DEPOSITS

What has been said above refers, strictly speaking, only to a crystal face of definite index. During the cathodic deposition of metals a polycrystalline deposit is usually formed, i.e., a deposit consisting of a large number of interconnected tiny single crystals or grains with faces of different index, a circumstance that complicates the picture. One of the complications involved is associated with the fact that different crystal faces grow at different rates and the nature of a deposit undergoes a change during electrolysis. To describe cathodic deposits one therefore utilizes, apart from the crystallographic structure, such concepts as growth structure, texture and the nature of the deposit.

By the growth structure is generally meant micro- and macroforms which a deposit assumes during growth. The most usual growth forms are: pyramidal, lamellar, and their combinations or derivatives—block (truncated pyramids), ribbed (a special case of the lamellar form with sharply defined ridges) and cubic (intermediate between the pyramidal and the lamellar form), and also the growth spirals mentioned earlier, whiskers (thin single threads) and dendrites (three-like deposits).

At small polarizations pyramids are often formed, which assume a lamellar structure with increasing polarization, and change into polycrystalline deposits or dendrites at still higher polarizations.

By texture is understood the preferential orientation of definite faces of polycrystal grains relative to some axis. What is most important in electrodeposition is the orientation relative to the axis normal to the cathode surface, i.e., the axis coinciding with the direction of growth of the deposit. If crystal faces show such an orientation, one speaks of a textured deposit and of a texture corresponding to the orientation of a definite face type. For instance, in the electrodeposition of copper from cyanide solutions the crystallites are not oriented and the deposit is not textured, but when copper is deposited from sulphate electrolytes the texture (011) is formed. In the case of nickel the texture (001) or (112) is observed when it is deposited from sulphate or chloride solutions, respectively. Texture is formed during electrodeposition and may be associated with the appearance of new faces which were absent at the initial stage of electrolysis. Since different faces are characterized by different exchange currents, during the formation of a deposit the elec-

trode potential may change at a constant current (or, conversely, the current may change at a constant potential).

The concept of the nature of a deposit covers a number of features such as monocrystallinity or polycrystallinity, orderliness or inhomogeneity, grain size—the fine-crystalline structure (the linear dimensions of crystallites not exceeding 10^{-5} cm) or the coarse-crystalline structure (the linear dimensions of grains being greater than 10^{-3} cm), etc. The term is used for qualitative description of metallic deposits.

15.4. TYPES OF PHASE OVERPOTENTIAL

In the case of the electrochemical formation of a crystalline phase the concept of phase overpotential, as follows from this chapter, is in fact a combination of several types of overpotential and it would therefore be more correct to call it *phase polarization.* In a general case the phase polarization is composed of three types of phase overpotential: the overpotential arising from the retarded formation of three-dimensional nuclei, η_3; the overpotential caused by the hindered formation of two-dimensional nuclei, η_2, and the overpotential due to the slow occurrence of surface diffusion, η_{sd}:

$$\Delta\varepsilon_{ph} = \eta_{ph} = \eta_3 + \eta_2 + \eta_{sd} \qquad (15.15)$$

The predominance of one or other type of phase overpotential depends on the deposit growth stage, i.e., on the time elapsed from the beginning of electrolysis, on the nature of the metal and the cathode substrate, the solution composition (and especially the nature and concentration of surface-active particles), the current intensity, temperature, etc.

CHAPTER 16

Electrochemical Overpotential

16.1. THE CONCEPT OF AN ELECTROCHEMICAL STEP

As has already been noted, any electrode process inevitably includes one or several steps at which particles either accept an electron (reduction reaction) or lose it (oxidation reaction).

The possible slow occurrence of this electrochemical step was first pointed out by Kolly (1880). The understanding of the causes responsible for the finite rate of this reaction step was greatly promoted by the works of LeBlanc (1910) and Izgaryshev (1915) which directed the attention of electrochemists to the important role of ionic hydration and dehydration in the kinetics of electrode processes. Kobozev and Nekrasov (1930) were the first to show, in their experiments on the cathodic evolution of hydrogen, that the state of particles immediately after they are discharged may differ essentially from the state of the final products of the electrode reaction. The rates of the discharge and ionization steps in the cathodic reaction of hydrogen evolution were measured by Dolin, Ershler and Frumkin (1940).

The earliest successful attempt at quantitative formulation of the theory of slow discharge was made by Erdey-Gruz and Volmer (1930), who deduced a formula relating the actual electrode potential to the current density. It is the basic equation of electrochemical overpotential, which is in accord with the empirical equation for hydrogen overpotential. However, the theory of slow discharge in its original form contained a number of insufficiently grounded assumptions and could not explain satisfactorily all the experimental facts. The major contribution to the slow-discharge theory was made by Frumkin (1933), who was the first to take into account the effect of the double-layer structure on the rate of electrochemical processes. These ideas largerly predetermined the basic trend in the development of the electrochemical science and the present state of the art.

Since the electrochemical act limits the rate of the overall electrode process, the current-induced deviation of the electrode potential is often called the *slow-discharge* (or *slow-ionization*) *overpotential.* Lately the term *charge-transfer overpotential* has come into use. But the essence of the electrochemical step does not reduce to the change of the valency state of particles (the discharge-ionization act) or to the transfer of charge across the electrode-electrolyte

interface. The gain (or loss) of an electron by a particle implies also the alteration of its physicochemical and energy state. For instance, in the course of the reaction

$$H_3O^+ + e = H_{ads} + H_2O$$

the gain of an electron by the particle H_3O^+ means that not only has the charge changed from $z_1 = 1$ to $z_2 = 0$ but also that the hydrated proton has become an adsorbed hydrogen atom, i.e., that the bond between the hydrogen ion and the solvent is broken up and a new one is formed between the hydrogen atom and the metal. The reduction of ferric ions to ferrous ions

$$Fe^{3+}xH_2O + e = Fe^{2+}yH_2O + (x - y)\,H_2O$$

involves the addition of one electron ($z = 1$), the change of the ionic charges from $z_1 = 3$ to $z_2 = 2$ and the rearrangement of the hydration sheath associated with the loss of $(x - y)$ water molecules. In the case of the reduction of vanadate to vanadyl

$$VO_3^- + e + 4H^+ = VO^{2+} + 2H_2O$$

the gain of an electron ($z = 1$) is accompanied by the change of the number of oxygen atoms in the ion (from three to one), its valency (from $n_1 = 5$ to $n_2 = 4$) and its charge (from $z_1 = -1$ to $z_2 = +2$). Here the number of electrons participating in the discharge step cannot be defined as the difference between the effective charges of the particles before and after the electrochemical act; in this case it corresponds to the difference between the valencies n_1 and n_2.

In the deposition of a metal from a solution of its simple salt the metallic ion divests itself of its hydration sheath and becomes an adatom (or adion)

$$M_{aq}^{z+} + ze = M_a + H_2O$$

which is then incorporated into the metal lattice.

It should be pointed out that the electrochemical deposition of metals may be regarded not as a discharge reaction with transfer of an electron from the cathode metal to the metallic ion in solution but as the transition of this ion from one phase (solution) to another (metal), its charge being compensated by the free electrons of the metal:

$$M_{aq}^{z+} + ze_{[M]} = [M] + H_2O$$

where $e_{[M]}$ represents an electron in the metallic phase.

Thus, the gain or loss of a charge by a particle is always accompanied by the rearrangement of its structure and the change of its nature. The more profound these changes, the higher must be the activation energy and the lower the rate of the electrochemical step, i.e., the greater the probability of this step determining the rate

of the overall electrode process and giving rise to an overpotential, which will be called hereafter the *electrochemical overpotential*[1] and denoted by η_e, or simply by η.

The theory of electrochemical overpotential was first developed for the cathodic evolution of hydrogen and later extended to other electrode processes. Until very recently this theory was based on the classical laws of the kinetics of heterogeneous chemical reactions. The quantitative relationships between the overpotential η and the current density i were obtained by applying the Brönsted principle of parallelism between the activation energy U and the thermal effect $\overline{Q}$ (or the free-energy change ΔG) for a series of similar reactions. The quantum-mechanical treatment of electrode processes began to emerge only recently although some attempts in this direction were undertaken in the middle of the 1930's (Gurney, Esin, and others). The bulk of investigations in this field have been carried out by Christov, Marcus, Levich and a number of other scientists. A review of the works on the quantum-mechanical theory of electrode processes is outside the scope of this book.

16.2. THE PRINCIPLES OF THE THEORY OF ELECTROCHEMICAL OVERPOTENTIAL

Originally, the theory of electrochemical overpotential implied conditions where the structure of the double layer and the distribution of the potential between its Helmholtz and diffuse parts could be ignored.

This assumption is justified (particularly in the region of low overpotentials) if the following conditions are satisfied.

1. Either the concentration of particles taking part in the electrochemical act is sufficiently high ($\geqslant 0.1$ mole/litre) or at any concentration of potential-determining particles the solution contains a large excess of foreign capillary-inactive electrolyte.
2. The solution contains no particles capable of being specifically adsorbed on the electrode.
3. The electrode potential is sufficiently remote from the zero point.

If these three conditions are fulfilled, the zeta potential is constant and small and its role in the electrode kinetics may therefore be ignored. These conditions are realizable in many practically important applications of electrochemical processes.

Further, the original version of the theory of electrochemical overpotential did not take into account that the nature of the par-

[1] Other terms which are widely used in the literature will also be employed to designate this type of overpotential.

ticles participating directly in the elementary electrochemical act may differ from the nature of the initial substances and final products of the electrochemical reaction.

Suppose that the discharge step is described by the equation

$$Ox + z_j F = R \tag{16.1}$$

where Ox represents particles which are near the electrode and are subjected to reduction by accepting z_j electrons, and R denotes particles formed immediately after the charge-transfer step. In the general case, the nature of particles Ox and R may differ from that of particles Ox^0 and R^0 involved in the overall electrode reaction

$$Ox^0 + zF = R^0$$

just as the equality $z = z_j$ may not be observed.

For instance, in the cathodic evolution of hydrogen the final products R^0 are hydrogen molecules and $z = 2$:

$$2H_3O^+ + 2e = H_2 + 2H_2O$$

and the elementary electrochemical act produces a hydrogen atom, which is adsorbed by the electrode, and $z_j = 1$:

$$H_3O^+ + e = H_{ads} + H_2O$$

In the deposition of a metal from complex electrolytes the composition of discharging ions (Ox) often differs from that of complex particles (Ox^0) predominating in the solution. Similarly, the elementary act of charge-transfer under the conditions of metal deposition gives rise to adatoms, which subsequently form a compact metal deposit. It should however be taken into account that when a purely electrochemical overpotential is responsible for the deviation of the electrode potential from the equilibrium value during the passage of a current, i.e.,

$$\Delta\varepsilon_i = \varepsilon_i - \varepsilon_r = \eta_e \tag{16.2}$$

all the other steps are considered reversible or practically reversible. Hence both the transition of the initial substances to the state of substances prior to the discharge act and the transformation of the particles resulting from the electrochemical act into the final products are also reversible. The concentration of particles Ox and R may be expressed in terms of the concentrations of initial Ox^0 and final R^0 particles with the aid of the equilibrium constants of the corresponding reactions.

The rate of electrochemical reaction (16.1) expressed in the units of current density in the forward $\vec{i}$ (reduction) and reverse $\overleftarrow{i}$ (oxidation) directions can be described by means of general kinetic equa-

tions:

$$\vec{i} = zFk_1c_{Ox} \tag{16.3}$$

and

$$\overleftarrow{i} = zFk_2c_R \tag{16.4}$$

But, in distinction to ordinary chemical reactions, the rate constants k_1 and k_2 in the electrochemical reactions are functions of the electrode potential. At equilibrium, i.e., at the reversible potential of the system, ε_r,

$$\vec{i} = \overleftarrow{i} = zFk_1^0c_{Ox} = zFk_2^0c_R = i^0 \tag{16.5}$$

where i^0 = exchange current at the electrochemical stage k_1^0 and k_2 = partial values of the rate constants at $\varepsilon = \varepsilon_r$. When the electrode potential departs from the equilibrium value in the negative or positive direction, assuming the value ε, reaction (16.1) will proceed predominantly in one direction at a rate i_ε determined by the equation

$$i_\varepsilon = \vec{i} - \overleftarrow{i} = zF\,({}_\varepsilon k_1 c_{Ox} - {}_\varepsilon k_2 c_R) \tag{16.6}$$

An assumption has been made that the activation energy of electrochemical reactions can be resolved into the chemical and the electrical component. The former corresponds to the case when the metal-solution potential difference g_{ML} is equal to zero; this component can be designated by U_0. The electrical component corresponds to the change of the activation energy due to the electric field in the double layer created by the potential difference g_{LM}; this component is denoted by ΔU_ε. Thus, Eqs. (16.3) and (16.4) may be written as follows

$$\vec{i} = zF_\varepsilon k_1 e^{-(\vec{U}_0 + \Delta\vec{U}_\varepsilon)/RT} \tag{16.7}$$

and

$$\overleftarrow{i} = zF_\varepsilon k_2 e^{(\overleftarrow{U}_0 + \Delta\overleftarrow{U}_\varepsilon)/RT} \tag{16.8}$$

If the potential difference g_{ML} is negative, the rate of the forward (cathodic) reaction must increase, and that of the backward (anodic) reaction decrease in proportion to the change of the electrical component of the activation energy. The energy of the electrical field, zFg_{ML}, is distributed between the two partial reactions. The distribution coefficient α characterizing the fraction of the double-layer energy that affects the forward reaction is known as the *transfer coefficient*. Assuming accordingly that the fraction of the energy required for the forward reaction is α and that for the backward reaction is $(1 - \alpha)$, one can write in place of Eqs. (16.7) and (16.8):

$$\vec{i} = zF_\varepsilon k_1 e^{-\vec{U}_0/RT} e^{-\alpha zFg_{ML}/RT} \tag{16.9}$$

and

$$\overleftarrow{i} = zFk_2 e^{-\overleftarrow{U}_0/RT} e^{(1-\alpha)zFg_{ML}/RT} \tag{16.10}$$

The difference in the signs of the second exponents in Eqs. (16.9) and (16.10) is attributable to the fact that, as mentioned before, the energy of the field accelerates one of the partial reactions and slows down the other. It follows from Eqs. (16.9) and (16.10) that when $g_{ML} < 0$ the rate of the forward process will increase and that of the backward reaction fall. When $g_{ML} = 0$, the partial currents $\vec{i}$ and $\overleftarrow{i}$ will not be equal and their difference

$$i_{g_{ML}=0} = (\vec{i} - \overleftarrow{i})_{g_{ML}=0}$$

must correspond to the rate of the chemical reaction proceeding under the conditions chosen (the concentrations of Ox and R, temperature, pressure, etc.), and catalyzed by the material of the electrode used. The value of g_{ML} cannot be determined experimentally, but it can be related to the measurable electrode potential on an arbitrary (e.g. hydrogen) scale with the aid of the equation

$$g_{ML} = \varepsilon + \text{const} \tag{16.11}$$

where the constant depends on the nature of the reference electrode. Using Eq. (16.11), one can rewrite Eqs. (16.9) and (16.10) as follows:

$$\vec{i} = zFk_1' c_{Ox} e^{-\vec{U}_0/RT} e^{-\alpha zF\varepsilon/RT} = zF\vec{k}c_{Ox} e^{-\alpha zF\varepsilon/RT} \tag{16.12}$$

and

$$\overleftarrow{i} = zFk_2' c_R e^{-\overleftarrow{U}_0/RT} e^{(1-\alpha)zF\varepsilon/RT} = zF\overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT} \tag{16.13}$$

whence

$$i = \vec{i} - \overleftarrow{i} = zF\left(kc_{Ox} e^{-\alpha zF\varepsilon/RT} - \overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT}\right) \tag{16.14}$$

If $\varepsilon = \varepsilon_r$, then

$$i = \vec{i} - \overleftarrow{i} = 0$$

or

$$\vec{i} = \overleftarrow{i} = zF\vec{k}c_{Ox} e^{-\alpha zF\varepsilon_r/RT} = zF\overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon_r/RT} \equiv i^0 \tag{16.15}$$

Since

$$\varepsilon_r = \varepsilon^0 + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_R}$$

then from Eq. (16.15) it follows that

$$i^0 = zF\vec{k}c_{Ox}^{(1-\alpha)} c_R^{\alpha} e^{-\alpha zF\varepsilon^0/RT} = zF\overleftarrow{k}c_{Ox}^{(1-\alpha)} c_R^{\alpha} e^{(1-\alpha)zF\varepsilon^0/RT} \tag{16.16}$$

or

$$i^0 = zFk^0 c_{Ox}^{(1-\alpha)} c_R^{\alpha} \tag{16.17}$$

where k^0 is the rate constant of reaction (16.1), which is given by the equation

$$k^0 = \vec{k} e^{-\alpha zF\varepsilon^0/RT} = \overleftarrow{k} e^{(1-\alpha)zF\varepsilon^0/RT}$$

The exchange current in Eq. (16.17) is a function of the concentration of particles Ox and R. If $c_{Ox} = 1$ and $c_R = 1$, then the partial exchange current corresponding to such unit concentrations is called the *standard exchange current* i_{st}^0 and serves as a kinetic characteristic of a given electrode reaction. Obviously,

$$i^0 = i_{st}^0 c_{Ox}^{(1-\alpha)} c_R^{\alpha} \tag{16.18}$$

Substituting the expressions for i^0 from Eq. (16.15) into Eqs. (16.12), (16.13) and (16.14), one has, respectively:

$$\vec{i} = i^0 e^{-\alpha zF\eta_e/RT} \tag{16.19}$$

$$\overleftarrow{i} = i^0 e^{(1-\alpha)\, zF\eta_e/RT} \tag{16.20}$$

and

$$i = \vec{i} - \overleftarrow{i} = i^0 \left(e^{-\alpha zF\eta_e/RT} - e^{(1-\alpha)\, zF\eta_e/RT}\right) \tag{16.21}$$

where $\eta_e = \varepsilon_i - \varepsilon_r$ is the electrochemical overpotential.

Equations (16.14) and (16.21) yield the following important special cases.

1. The electrode potential is equal to its equilibrium value, i.e., $\varepsilon = \varepsilon_r$. Then

$$i = 0 \quad \text{and} \quad \vec{i} = \overleftarrow{i}$$

and

$$zF\vec{k}c_{Ox}e^{-\alpha zF\varepsilon_r/RT} = zF\overleftarrow{k}c_R e^{(1-\alpha)\, zF\varepsilon_r/RT} \tag{16.22}$$

Solving Eq. (16.22) for ε_r, one gets the Nernst equation for the reversible electrode potential[1]:

$$\varepsilon_r = \frac{RT}{zF} \ln \frac{\vec{k}}{\overleftarrow{k}} + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_R} = \frac{RT}{zF} \ln k + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_R} =$$

$$= \varepsilon^0 + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_R} \tag{16.23}$$

2. The system departs but very slightly from the equilibrium state and the overpotential is small and corresponds to the inequality $zF\eta < RT$. In this case each exponent in Eq. (16.21) can be expanded

[1] Here the difference between Ox and R, on the one hand, and between Ox^0, and R^0, on the other, is ignored.

into a series, only the first two terms being retained:

$$e^{-\alpha zF\eta/RT} = 1 - \frac{\alpha zF\eta}{RT}$$

and

$$e^{(1-\alpha)zF\eta/RT} = 1 + \frac{(1-\alpha)\,zF\eta}{RT}$$

Then

$$\underset{\eta\to 0}{i} = \vec{i} - \overleftarrow{i} = -i^0 \frac{zF}{RT}\,\eta \tag{16.24}$$

or

$$\eta = -\frac{RT}{zF} \cdot \frac{i}{i^0} \tag{16.25}$$

Equations (16.24) and (16.25) show that in the region of small overpotentials a linear relationship between η and i is observed. The quantity $(RT/zF)\cdot(1/i^0)$ is a kinetic analog of the resistance in Ohm's formula and is called the *polarization resistance* R_e at the electrochemical overpotential:

$$R_e = \frac{RT}{zF} \cdot \frac{1}{i^0} \tag{16.26}$$

The value of R_e corresponds to the derivative of the overpotential with respect to current at $\eta \to 0$, i.e.,

$$\left(\frac{\partial\eta}{\partial i}\right)_{\eta\to 0} = -\frac{RT}{zF} \cdot \frac{1}{i^0} = +R_e \tag{16.27}$$

Using the quantity R_e, one can write in place of Eq. (16.25)

$$\eta = R_e i \tag{16.28}$$

3. The system departs markedly from equilibrium and a high current i passes through it. If $\vec{i} \gg \overleftarrow{i}$, i.e., the cathodic process occurs, the second term in Eq. (16.14) may be neglected as compared with the first term and i_c defined as a function of the potential with the aid of Eq. (16.12):

$$i_c = \vec{i} = zF\vec{k}c_{\mathrm{Ox}}e^{-\alpha zF\varepsilon/RT}$$

or

$$\varepsilon_i = \frac{RT}{\alpha zF} \ln zF\vec{k} + \frac{RT}{\alpha zF} \ln c_{\mathrm{Ox}} - \frac{RT}{\alpha zF} \ln i_c \tag{16.29}$$

For the same conditions Eq. (16.21) yields

$$i_c = \vec{i} = i^0 e^{-\alpha zF\eta/RT}$$

or

$$\eta = \frac{RT}{\alpha zF} \ln i^0 - \frac{RT}{\alpha zF} \ln i_c \tag{16.30}$$

Introducing the notations

$$2.3 \frac{RT}{\alpha zF} \log i^0 = a_c \tag{16.31}$$

and

$$-2.3 \frac{RT}{\alpha zF} = b_c \tag{16.32}$$

Eq. (16.30) can be rewritten in the form

$$\eta = a_c + b_c \log i \tag{16.33}$$

Equation (16.33) based on different assumptions was first derived by Tafel (1905) and is known as *Tafel's equation*; the quantities a_c and b_c are called *Tafel constants.*

Equation (16.33) can also be arrived at from the definition of overpotential:

$$\eta = \varepsilon_i - \varepsilon_r$$

by substituting the values of ε_i and ε_r from Eqs. (16.29) and (16.23), respectively.

For the case $\vec{i} \ll \overleftarrow{i}$, i.e., when the anodic process takes place, $i = -i_a = -\overleftarrow{i}$ and the first term in Eq. (16.21) may be ignored as compared with the second:

$$i_a = i^0 e^{(1-\alpha)zF\eta/RT} \tag{16.34}$$

or

$$\eta = -\frac{RT}{(1-\alpha)\,zF} \ln i^0 + \frac{RT}{(1-\alpha)\,zF} \ln i_a \tag{16.35}$$

Introducing the notations

$$-2.3 \frac{RT}{(1-\alpha)\,zF} \ln i^0 = a_a$$

and

$$2.3 \frac{RT}{(1-\alpha)\,zF} = b_a$$

Eq. (16.35) is transformed into Tafel's equation for the anodic process

$$\eta = a_a + b_a \log i \tag{16.36}$$

16.3. THE THEORY OF ELECTROCHEMICAL OVERPOTENTIAL WITH ACCOUNT TAKEN OF THE DOUBLE-LAYER STRUCTURE

At the charge-transfer step, the slow rate of which gives rise to an electrochemical overpotential, a special role is played by the double-layer structure at the interface between two phases. Indeed,

while other steps of the electrode process, e.g. the transport of particles or the homogeneous chemical transformation, take place far away from the double layer, though near the electrode-electrolyte interface, the electrochemical act proper occurs within the double layer. The distribution of the potential in the double layer and the position of the reacting particles in it must therefore affect markedly the rate of the electrochemical act and the electrochemical overpotential. Frumkin, who was the first to put forward this idea, formulated it quantitatively on the basis of certain assumptions. The first assumption is that the actually existing double layer can be satisfactorily described by the Stern model. According to the second assumption the electrochemical act involves only those particles which reside in the Helmholtz part of the double layer, i.e., in the immediate vicinity of the electrode. In consequence, the average energy of charged particles and their concentration near the electrode surface must be different from those in the bulk of the solution, this difference being caused by the potential difference ζ in the diffuse part of the double layer.

A slightly modified derivation of Frumkin's formula for the electrochemical overpotential as suggested by Parsons and Delahay is given below.

Let the overall electrode reaction be described by Eq. (16.1):

$$\mathrm{Ox} + zF = \mathrm{R}$$

the charge of particles Ox and R being z_1 and z_2, respectively, and $z = z_1 - z_2$. To simplify matters, it may be assumed that all z charges are transferred during a single electrochemical act, i.e., that $z = z_e$. For convenience, it is advisable to split up reaction (16.1) with respect to time (or, more generally, with respect to the reaction coordinate) into steps differing in the nature of the particles present and in their position relative to the electrode-electrolyte interface (see Fig. 16.1). Each step has its own value of the free energy of the system (16.1). These steps are as follows.

1. Reaction (16.1) has not yet started. The solution in the system contains particles Ox (beyond the confines of the double layer) and z electrons are inside the metal (Fig. 16.1*a*). If the potential of the metal is referred to the point in the bulk of the solution where it is taken to be zero, the standard free energy of the system under consideration in this state, G_{I}^0, will then be equal to

$$G_{\mathrm{I}}^0 = \mu_{\mathrm{L}}^{\mathrm{Ox}} + z\mu_{[\mathrm{M}]}^{e} - zFg_{\mathrm{LM}} \qquad (16.37)$$

Particles Ox have a charge of z_1, but since there is no potential at their site, Eq. (16.37) includes only their chemical potential $\mu_{\mathrm{L}}^{\mathrm{Ox}}$ in the solution. The energy of electrons in the metal is characterized by the sum of their chemical potential $\mu_{[\mathrm{M}]}^{e}$ and electrical component zFg_{ML}, where g_{ML} is the metal-solution Galvani potential.

2. Having crossed the site of the ζ potential drop, particles Ox entered the double layer and found themselves in its Helmholtz portion; the reaction has not yet occurred and the z electrons are

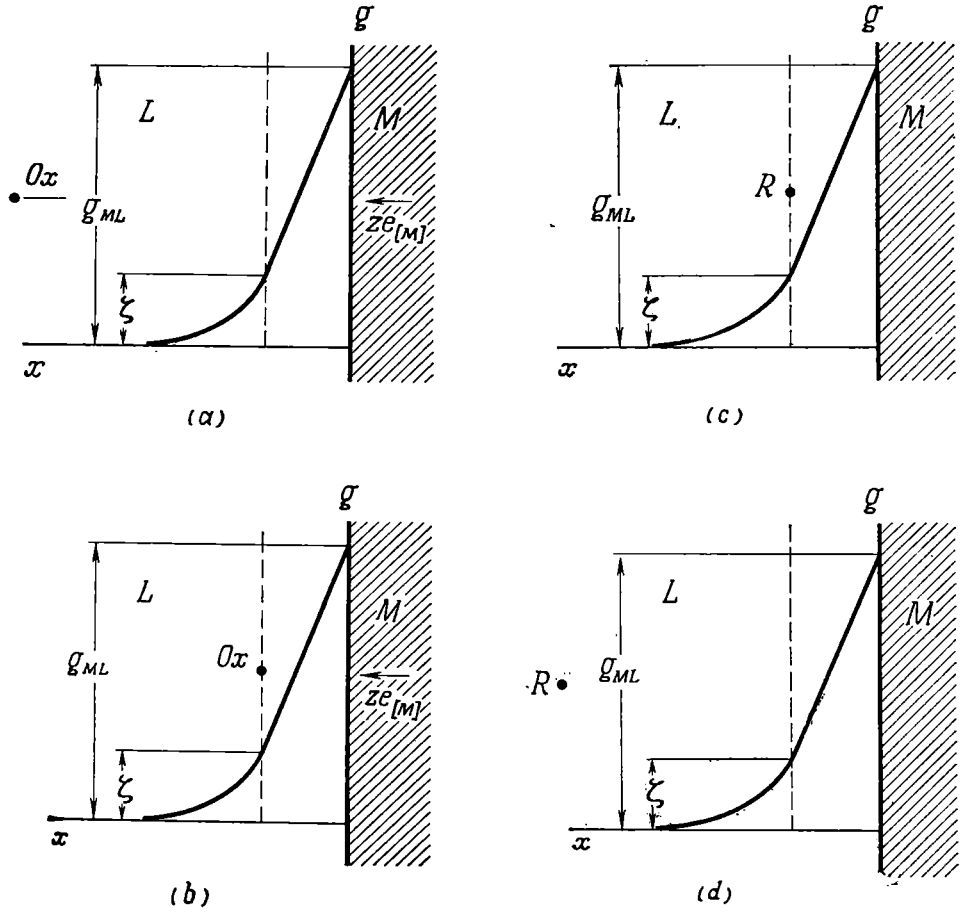

Fig. 16.1. The sequence of steps for the reaction $Ox + zF = R$

still in the metal. The free energy of the second step, G^0_{II} (Fig. 16.1*b*), is therefore determined by the equation

$$G^0_{II} = \mu^{Ox}_{LII} + z_1 F\zeta + z\mu^e_{[M]} - zFg_{ML} \qquad (16.38)$$

where the subscript LII signifies the Helmholtz portion of the double layer in the solution.

3. An activated complex is formed. The standard free energy of this transition state is equal to

$$G^0_{III} = G^0_* \qquad (16.39)$$

4. Having added on the z electrons (the metal now contains no reacting electrons), particles Ox are transformed into particles R in the Helmholtz part of the double layer (Fig. 16.1*c*). In accordance

with this the standard free energy G^0_{IV} is given by the equation

$$G^0_{IV} = \mu^R_{LII} + z_2 F\zeta \tag{16.40}$$

5. Particles R have gone beyond the double layer (Fig. 16.1*d*). The standard free energy G^0_V is equal to the chemical potential of these particles:

$$G^0_V = \mu^R_L \tag{16.41}$$

To describe the kinetics of the electrochemical transformation Parsons and Delahay make use of the Glasstone-Eyring-Laidler theory of the absolute rates of chemical reactions. For electrochemical processes the rate of the forward reaction is written as

$$\vec{i} = xzF \frac{kT}{h} c_{Ox} e^{-\Delta\vec{G}^0/RT} \tag{16.42}$$

and that of the reverse reaction

$$\overleftarrow{i} = xzF \frac{kT}{h} c_R e^{-\Delta\overleftarrow{G}^0/RT} \tag{16.43}$$

where x = transmission coefficient (transmissivity) determining the probability of occurrence of the process; it is usually taken as equal to unity: $x = 1$

k = Boltzmann constant

h = Planck constant

$\vec{G}^0$ and $\overleftarrow{G}^0$ = standard activation energies of reaction (16.1) in the forward and reverse directions, respectively.

The quantity $\Delta\vec{G}^0$ is defined as the difference between the energies in the transitional and initial (first) states

$$\Delta\vec{G}^0 = G^0_* - G^0_I \tag{16.44}$$

and $\Delta\vec{G}^0$ as the difference between the energies in the transitional and final (fifth) states:

$$\Delta\vec{G}^0 = G^0_* - G^0_V \tag{16.45}$$

The quantity G^0_* does not yet lend itself to calculation and therefore more or less realistic assumptions are made to find the values of $\Delta\vec{G}^0$ and $\Delta\overleftarrow{G}^0$. For instance, since in a general case the free energy is equal to the sum of the electrochemical potentials of all particles with corresponding stoichiometric numbers

$$G^0 = \Sigma\nu_j\mu_{j(ech)} \tag{16.46}$$

it can be decomposed into the chemical and electrical components:

$$G^0 = \Sigma\nu_j\mu_j + \Sigma\nu_j z_j F g_{ML} = G^0_{ch} + G^0_e \tag{16.47}$$

The activation energy can also be represented as the sum of chemical and electrical energies, i.e.,

$$\vec{\Delta G}^0 = \vec{\Delta G}^0_{ch} + \vec{\Delta G}^0_e \tag{16.48}$$

and

$$\overleftarrow{\Delta G}^0 = \overleftarrow{\Delta G}^0_{ch} + \overleftarrow{\Delta G}^0_e \tag{16.49}$$

Similar equations are also valid for all quantities characterizing the various steps of reaction (16.1):

$$G^0_{\mathrm{I}} = G^0_{\mathrm{I}ch} + G^0_{\mathrm{I}e} = G^0_{\mathrm{I}ch} + (-zFg_{\mathrm{LM}}) \tag{16.50}$$

$$G^0_{\mathrm{II}} = G^0_{\mathrm{II}ch} + G^0_{\mathrm{II}e} = G^0_{\mathrm{II}ch} + z_1F\zeta + (-zFg_{\mathrm{ML}}) \tag{16.51}$$

$$G^0_{\mathrm{III}} = G^0_* = G^0_{*ch} + G^0_{*e} \tag{16.52}$$

$$G^0_{\mathrm{IV}} = G^0_{\mathrm{IV}ch} + G^0_{\mathrm{IV}e} + G^0_{\mathrm{IV}ch} + z_2F\zeta \tag{16.53}$$

$$G^0_{\mathrm{V}} = G^0_{\mathrm{V}ch} + G^0_{\mathrm{V}e} = G^0_{\mathrm{V}ch} \tag{16.54}$$

On the basis of Eqs. (16.48) and (16.50) one can now rewrite Eq. (16.44) as follows:

$$\vec{\Delta G}^0 = G^0_* - G^0_{\mathrm{I}} = \vec{\Delta G}^0_{ch} + G^0_{*e} - G^0_{\mathrm{I}e} \tag{16.55}$$

or, adding and subtracting $G^0_{\mathrm{II}e}$,

$$\vec{\Delta G}^0 = \vec{\Delta G}^0_{ch} + G^0_{*e} - G^0_{\mathrm{II}e} + (G^0_{\mathrm{II}e} - G^0_{\mathrm{I}e}) \tag{16.56}$$

Parsons and Delahay assume further that the difference between the electrical components of free energies in the transitional and second states constitutes a certain fraction α $(0 \leqslant \alpha \leqslant 1)$ of the difference between the electrical components of free energies in the fourth and second states:

$$G^0_{*e} - G^0_{\mathrm{II}e} = \alpha\,(G^0_{\mathrm{IV}e} - G^0_{\mathrm{II}e}) \tag{16.57}$$

Combining Eqs. (16.56) and (16.57), one obtains

$$\vec{\Delta G}^0 = \Delta G^0_{ch} + \alpha\,(G^0_{\mathrm{IV}e} - G^0_{\mathrm{II}e}) + (G^0_{\mathrm{II}e} - G^0_{\mathrm{I}e}) \tag{16.58}$$

or, after substituting the values of the electrical components from Eqs. (16.50), (16.51), and (16.53),

$$\vec{\Delta G}^0 = \vec{\Delta G}^0_{ch} + \alpha\,(z_2F\zeta - z_1F\zeta + zFg_{\mathrm{ML}}) + (z_1F\zeta - zFg_{\mathrm{ML}} + zFg_{\mathrm{ML}}) = \vec{\Delta G}^0_{ch} + \alpha zFg_{\mathrm{ML}} - (\alpha z - z_1)\,F\zeta \tag{16.59}$$

Similar reasoning for $\vec{\Delta G}^0$ yields

$$\overleftarrow{\Delta G}^0 = \overleftarrow{\Delta G}^0_{ch} - (1-\alpha)\,zFg_{\mathrm{ML}} - (\alpha z - z_1)\,F\zeta \tag{16.60}$$

Taking into account Eqs. (16.59) and (16.60), one can now rewrite Eqs. (16.42) and (16.43) as follows:

$$\vec{i} = xzF \frac{kT}{h} c_{Ox} e^{-\Delta \vec{G}^0_{ch}/RT} e^{-\alpha z F g_{ML}/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.61}$$

and

$$\overleftarrow{i} = xzF \frac{kT}{h} c_R e^{-\Delta \overleftarrow{G}^0_{ch}/RT} e^{(1-\alpha)zF g_{ML}/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.62}$$

Since $x = 1$ and

$$g_{ML} = \varepsilon + \text{const}$$

where ε is the electrode potential on an arbitrary scale, e.g. on the hydrogen scale, it follows that

$$\vec{i} = zF \frac{kT}{h} c_{Ox} e^{-\Delta G^0_{ch}/RT} e^{-\alpha zF \text{ const}/RT} e^{-\alpha zF\varepsilon/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.63}$$

and

$$\overleftarrow{i} = zF \frac{kT}{h} c_R e^{-\Delta G^0_{ch}/RT} e^{(1-\alpha)zF \text{ const}/RT} e^{(1-\alpha)zF\varepsilon/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.64}$$

If all the quantities independent of potential and concentration are lumped into constants, then, in place of Eqs. (16.63) and (16.64), one can write:

$$\vec{i} = zF\vec{k}c_{Ox} e^{-\alpha zF\varepsilon/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.65}$$

and

$$\overleftarrow{i} = zF\overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT} e^{(\alpha z - z_1)F\zeta/RT} \tag{16.66}$$

The net current passing through the electrode at a given potential ε is given by

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT} (\vec{k}c_{Ox} e^{-\alpha zF\varepsilon/RT} - \overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT}) \tag{16.67}$$

The difference between this equation and the corresponding equation (16.14), which has been derived without taking into account the double-layer structure, is that the former contains the factor $e^{(\alpha z - z_1)F\zeta/RT}$. If $\zeta = 0$ or $(\alpha z - z_1) = 0$, then Eq. (16.67) changes to Eq. (16.14).

From Eq. (16.67), after substituting $\varepsilon = \varepsilon_r + \eta$, we obtain:

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT} (\vec{k}c_{Ox} e^{-\alpha zF\varepsilon_r/RT} e^{-\alpha zF\eta/RT} - \\ - \overleftarrow{k}c_R e^{(1-\alpha)F\varepsilon_r/RT} e^{(1-\alpha)zF\eta/RT})$$

or

$$i = \vec{i} - \overleftarrow{i} = i^0 e^{(\alpha z - z_1)F\zeta/RT} (e^{-\alpha zF\eta/RT} - e^{(1-\alpha)zF\eta/RT}) \tag{16.68}$$

For definite regions of ε and η values Eqs. (16.67) and (16.68) yield formulas coinciding in appearance either with the Nernst equation ($\varepsilon = \varepsilon_r$ or $\eta = 0$) or with Ohm's law ($zF\varepsilon/RT \ll 1$ or $zF\eta/RT \ll 1$). Here we shall consider the third special case in which reaction (16.1) proceeds predominantly in one direction. If the process occurring at the electrode is reduction, then $\vec{i} \gg \overleftarrow{i}$ and

$$i = i_c = \vec{i} = i^0 e^{(\alpha z - z_1)F\zeta/RT} e^{-\alpha zF\eta/RT} \tag{16.69}$$

or, after taking logarithms,

$$\ln i_c = \ln i^0 + \frac{(\alpha z - z_1)F\zeta}{RT} - \frac{\alpha zF\eta}{RT} \tag{16.70}$$

Solving Eq. (16.70) for the overpotential gives

$$\eta = \frac{RT}{\alpha zF} \ln i^0 + \frac{(\alpha z - z_1)\zeta}{\alpha z} - \frac{RT}{\alpha zF} \ln i_c \tag{16.71}$$

According to Eq. (16.18), the exchange current is a function of the concentration of reactants in the electrode process:

$$i^0 = i^0_{st} c_{\mathrm{Ox}}^{(1-\alpha)} c_{\mathrm{R}}^{\alpha}$$

and, consequently,

$$\eta = \frac{RT}{\alpha zF} \ln i^0_{st} + \frac{RT}{zF} \cdot \frac{(1-\alpha)}{\alpha} \ln c_{\mathrm{Ox}} + \frac{RT}{zF} \ln c_{\mathrm{R}} + \\ + \frac{(\alpha z - z_1)\zeta}{\alpha} - \frac{RT}{\alpha zF} \ln i_c \tag{16.72}$$

At $\alpha = 0.5$ and $z = z_1 = 1$ Eq. (16.72) simplifies to

$$\eta = 2\frac{RT}{F} \ln i^0_{st} + \frac{RT}{F} \ln c_{\mathrm{Ox}} + \frac{RT}{F} \ln c_{\mathrm{R}} + \zeta - 2\frac{RT}{F} \ln i_c \tag{16.73}$$

This equation corresponds to the formula derived by Frumkin for the cathodic evolution of hydrogen. From Frumkin's formula it follows that the overpotential depends not only on the concentration of the direct participants of the electrode reaction but also on the nature and content of any substances present, primarily surface-active substances, which may affect the ζ potential. For the special case $\zeta = 0$ Eq. (16.73) takes the form of the Erdey-Gruz-Volmer formula.

16.4. APPLICATION OF GENERAL EQUATIONS OF ELECTROCHEMICAL OVERPOTENTIAL TO THE MOST WIDESPREAD ELECTRODE REACTIONS

Equation (16.67) and its special case—Eq. (16.14)—have been derived specifically for reaction (16.1):

$$\mathrm{Ox} + zF = \mathrm{R}$$

under the assumption that both its participants are charged and are present in the electrolyte in dissolved state. It is therefore natural

that for all ion recharging reactions such as

$$Fe^{3+} + e = Fe^{2+}$$
$$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}, \text{ etc.}$$

Eq. (16.67) can be applied without any changes. For example, in the case of reduction of ferric ions to ferrous ions it can be written as

$$i = \vec{i} - \overleftarrow{i} = Fe^{(\alpha-3)F\zeta/RT}(\vec{k}c_{Fe^{3+}} + e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}c_{Fe^{2+}}e^{(1-\alpha)F\varepsilon/RT}) \tag{16.74}$$

since

$$c_{Ox} = c_{Fe^{3+}}, \quad c_R = c_{Fe^{2+}}, \quad z = 1, \quad \text{and} \quad z_1 = 3$$

When the metallic ions are discharged at the mercury electrode to form the corresponding amalgam, $c_{Ox} = c_{Mz+}$ and $c_R = c_{M(Hg)}$, where $c_{M(Hg)}$ is the concentration of the metal in the amalgam. For instance, for deposition of sodium on a sodium amalgam

$$Na^+ + e \underset{}{\overset{Hg}{\rightleftharpoons}} Na(Hg) \tag{16.75}$$

the electrochemical overpotential will be described by the equation

$$i = \vec{i} - \overleftarrow{i} = Fe^{(\alpha-1)F\zeta/RT}(\vec{k}c_{Na^+}e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}c_{Na(Hg)}e^{(1-\alpha)F\varepsilon/RT}) \tag{16.76}$$

If the metal is deposited on a solid cathode, the discharge of ions will at first produce adatoms of the metal (or its adions), and only then (at the next stage) are they incorporated into the metal lattice. In this case $c_{Ox} = c_{M^{z+}}$ and $c_R = c_{M(a)}$, where $c_{M(a)}$ is the adatom concentration on the metal. If the surface concentration of adatoms is very low, then the entire cathode surface may be considered active and Eq. (16.67) can be written in its usual form. For instance, in the deposition of zinc on a zinc electrode

$$Zn^{2+} + e = Zn_a = [Zn]$$

the electrochemical overpotential is described by the equation

$$i = \vec{i} - \overleftarrow{i} = 2Fe^{(2\alpha-2)F\zeta/RT} \times (\vec{k}c_{Zn^{2+}}e^{-2\alpha F\varepsilon/RT} - \overleftarrow{k}c_{Zn(a)}e^{2(1-\alpha)F\varepsilon/RT}) \tag{16.77}$$

In case the reduction (or oxidation) products are adsorbed on the electrode, thereby blocking a perceptible part of its surface equal to θ which can no longer be ignored, Eq. (16.67) must be modified in conformity with the kinetic peculiarities of a particular electrode reaction. This case is best illustrated by considering the cathodic

evolution of hydrogen from acidic and alkaline solutions:

$$H_3O^+ + e = H_{ads} + H_2O \qquad (16.78)$$

$$H_2O + e = H_{ads} + OH^- \qquad (16.79)$$

As a result of an electrochemical act, atomic hydrogen is formed, which is adsorbed on the cathode. At a given current density the coverage of the electrode surface by hydrogen atoms constitutes a certain value θ'_H. If the electrode polarization is caused only by the slow occurrence of the electrochemical step, all other steps, including the removal of the adsorbed hydrogen, proceed at much higher rates than the charge-transfer step and hence the coverage at the given current must be equal (or almost equal) to the coverage θ_H in the absence of external current, i.e., at the equilibrium potential of the hydrogen electrode: $\theta'_H = \theta_H$. It may be assumed that the hydrogen ions are discharged only on that part of the surface $(1 - \theta_H)$ which is free of adsorbed hydrogen atoms. The rates of hydrogen evolution from acidic solutions ($z_1 = 1$, $z = 1$) and from alkaline solutions ($z_1 = 0$, $z = 1$) will then obey the following equations, respectively,

$$i = \vec{i} - \overleftarrow{i} = Fe^{(\alpha-1)F\zeta/RT}[\vec{k}c_{H_3O^+}(1 - \theta_H)\, e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}c_{H_2O}\theta_H e^{(1-\alpha)F\varepsilon/RT}] \qquad (16.80)$$

$$i = \vec{i} - \overleftarrow{i} = Fe^{\alpha F\zeta/RT}[\vec{k}c_{H_2O}(1 - \theta)\, e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}c_{OH^-}\theta_H e^{(1-\alpha)F\varepsilon/RT}] \qquad (16.81)$$

This mechanism of hydrogen evolution is often called the *Volmer-Frumkin mechanism.*

Another possible path of hydrogen evolution is the discharge of hydrogen ions or water molecules on already adsorbed hydrogen atoms:

$$H_3O^+ + H_{ads} + e = H_2 + H_2O \qquad (16.82)$$

for acidic solutions and

$$H_2O + H_{ads} + e = H_2O + OH^- \qquad (16.83)$$

for alkaline solutions.

Kinetic equations corresponding to reactions (16.82) and (16.83) are of the following form

$$i = \vec{i} - \overleftarrow{i} = Fe^{(\alpha-1)F\zeta/RT}[\vec{k}c_{H_3O^+} + \theta_H e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}p_{H_2}c_{H_2O}(1 - \theta_H)\, e^{(1-\alpha)F\varepsilon/RT}] \qquad (16.84)$$

and

$$i = \vec{i} - \overleftarrow{i} = Fe^{\alpha F\zeta/RT}\,[\vec{k}c_{H_2O}\theta_H e^{-\alpha F\varepsilon/RT} - \\ - \overleftarrow{k}p_{H_2}c_{OH^-}(1-\theta_H)\,e^{(1-\alpha)F\varepsilon/RT}] \quad (16.85)$$

This mechanism of hydrogen evolution is known as the *Heyrovsky-Horuiti mechanism.*

16.5. SUPERPOSITION OF CONCENTRATION POLARIZATION UPON ELECTROCHEMICAL OVERPOTENTIAL

It has been thought until now that the deviation of the electrode potential from the equilibrium value is wholly due to some single cause and the electrode polarization is quite a definite type of overpotential. In real conditions it would be more correct to speak of the predominance of one type of overpotential. Other types of overpotential are superimposed to a greater or lesser degree on the main overpotential. More often than not concentration polarization is superimposed on the electrochemical or phase overpotential. In this case the departure of the potential from the equilibrium value will be the sum of two or more types of overpotential; the activation polarization itself also changes under concentration limitations (as compared with similar conditions—say, at the same current density, but in the absence of concentration polarization).

If the general equation of electrochemical overpotential (16.67) is used, the equilibrium values of c_{Ox} and c_R should in this case be replaced by c'_{Ox} and c'_R, which have been changed as a result of the hindered transport step and correspond now to the given current density, i.e.,

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT}\,(\vec{k}c'_{Ox}e^{-\alpha zF\varepsilon/RT} - \\ - \overleftarrow{k}c'_R e^{(1-\alpha)zF\varepsilon/RT}) \quad (16.86)$$

or, after multiplying and dividing the first and second terms in parentheses by c_{Ox} and c_R, respectively,

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT}\left(\vec{k}\,\frac{c'_{Ox}}{c_{Ox}}\,c_{Ox}e^{-\alpha zF\varepsilon/RT} - \overleftarrow{k}\,\frac{c'_R}{c_R}\,c_R e^{(1-\alpha)zF\varepsilon/RT}\right) \quad (16.87)$$

When $\varepsilon = \varepsilon_r$, then $\vec{i} = \overleftarrow{i} = i^0$ and hence

$$i = \vec{i} - \overleftarrow{i} = i^0\left(\frac{c'_{Ox}}{c_{Ox}}\,e^{\alpha zF(\eta_e+\eta_d)/RT} - \frac{c'_R}{c_R}\,e^{(1-\alpha)zF(\eta_e+\eta_d)/RT}\right) \quad (16.88)$$

where the electrode polarization is the sum of the electrochemical overpotential η_e and the transport overpotential η_d, and $i^{0\prime} = i^0 e^{(\alpha z - z_1)F\zeta/RT}$. Denoting $\eta_e + \eta_d = \eta$ and recalling that accord-

ing to Eq. (14.29)

$$\frac{c'_{Ox}}{c_{Ox}} = 1 - \frac{i}{c i_l} \text{ and } \frac{c'_R}{c_R} = 1 + \frac{i}{c i_l}$$

one can write, in place of Eq. (16.88),

$$i = \vec{i} - \overleftarrow{i} = i^0 \left[\left(1 - \frac{i}{c i_l}\right) e^{-\alpha z F\eta/RT} - \left(1 + \frac{i}{c i_l}\right) e^{(1-\alpha)\, zF\eta/RT} \right] \quad (16.89)$$

Solving Eq. (16.89) for i yields the equation

$$i = i^{0\prime} \frac{e^{-\alpha z F\eta/RT} - e^{(1-\alpha) zF\eta/RT}}{1 + \frac{i^{0\prime}}{c i_l} e^{-\alpha z F\eta/RT} + \frac{i^{0\prime}}{a i_l} e^{(1-\alpha)\, zF\eta/RT}} \quad (16.90)$$

A number of special cases emerge from Eq. (16.90). For example, if $i^{0\prime} t \ll {}_c i_l$ and $i^{0\prime} \ll {}_a i_l$, then

$$i = i^0 e^{(\alpha z - z_1) F\zeta/RT} \left(e^{-\alpha z F\eta/RT} - e^{(1-\alpha) zF\eta/RT}\right)$$

which corresponds to the purely electrochemical overpotential and $\eta = \eta_e$.

If $i^{0\prime} \gg {}_c i_l$ and $i^{0\prime} \gg {}_a i_l$, ${}_c i_l$ being much smaller than ${}_a i_l$, then Eq. (16.90) simplifies to

$$i = ({}_c i_l - {}_c i_l e^{zF\eta/RT}) = {}_c i_l (1 - e^{zF\eta/RT}) \quad (16.91)$$

which corresponds to a purely diffusion overpotential and $\eta = \eta_d$.

The superposition of the reaction and electrochemical overpotentials can be illustrated by considering the discharge of hydroxonium ions according to scheme (16.78). In the derivation of Eq. (16.80). which determines the rate of this process, it was assumed that the step at which the adsorbed hydrogen atoms are removed proceeds unhindered. If, however, this step proceeds at a finite rate, then the coverage of the surface by adsorbed atoms at each current density value will differ from the equilibrium value, i.e., $\theta'_H \neq \theta_H$. In this case one should write, in place of Eq. (16.80),

$$i = \vec{i} - \overleftarrow{i} = F e^{(\alpha-1)F\zeta/RT} [\vec{k} c_{H_3O^+} (1 - \theta'_H)\, e^{-\alpha F\varepsilon'/RT} - \\ - \overleftarrow{k} c_{H_2O} \theta'_H e^{(1-\alpha)F\varepsilon'/RT}] \quad (16.92)$$

Dividing and multiplying the first and second terms in parentheses by $1 - \theta_H$ and θ_H, respectively, and introducing the notation

$$i^0 = \vec{k} c_{H_3O^+} + (1 - \theta_H)\, e^{-\alpha F\varepsilon_r/RT} = \overleftarrow{k} c_{H_2O} (1 - \theta_H)\, e^{(1-\alpha)F\varepsilon_r/RT} \quad (16.93)$$

one can rewrite Eq. (16.80) in the form

$$i = i^{0\prime} e^{(\alpha-1)F\zeta/RT} \left(\frac{1 - \theta'_H}{1 - \theta_H} e^{-\alpha F\eta/RT} - \frac{\theta'_H}{\theta_H} e^{(1-\alpha)F\eta/RT}\right) \quad (16.94)$$

where $\eta = \eta_e + \eta_r$, i.e., η is the sum of the electrochemical and reaction overpotentials.

From Eqs. (16.92) and (16.94) it follows that the kinetics of electrode processes depends on the coverage of the surface by hydrogen atoms.

16.6. MULTISTEP ELECTROCHEMICAL REACTIONS

It was assumed until now that the electrochemical reaction consists of only one step, i.e., that the z electrons participating in it are transferred all at once. This is valid only when $z = 1$, i.e., when only one electron is involved in the reaction. If $z = 2$, then two variants are possible: either simultaneous transfer of both electrons, or a two-step electrochemical reaction, one electron being transferred at each step. When $z > 2$, the number of possible versions becomes still larger. For instance, if $z = 3$, all the three electrons may be transferred at one time, which however is highly improbable. A more probable version is a sequence of one-electron transfers, i.e., a three-step reaction. Retardation at these steps may be different, and one of them, the slowest, will limit the rate of the overall electrode reaction.

The simplest example of such consecutive (i.e., multistep) electrochemical reactions is a two-step act, when $z = 2$ and the overall electrode reaction consists of two one-electron transfers:

$$\mathrm{Ox} + e = \mathrm{M} \tag{16.95a}$$

$$\mathrm{M} + e = \mathrm{R} \tag{16.95b}$$

where M is a certain intermediate product. Each of these transfers occurs independently of the other. Though only one step is rate-determining, under stationary conditions all the transformations will proceed at the same rate and therefore the net current

$$i = zi'_j$$

where i'_j is the current corresponding to the rate-determining step. In the case under consideration

$$i = 2i'_j$$

These two steps are described by the following kinetic equations, respectively,

$$\frac{i}{2} = i_a = i_a^0 \left(e^{-\alpha_a F\eta/RT} - \frac{c'_{\mathrm{M}}}{c_{\mathrm{M}}} e^{(1-\alpha_a)F\eta/RT} \right)$$

and

$$\frac{i}{2} = i_b = i_b^0 \left(\frac{c'_{\mathrm{M}}}{c_{\mathrm{M}}} e^{-\alpha_b F\eta/RT} - e^{(1-\alpha_b)F\eta/RT} \right)$$

where a refers to the first reaction step (16.95a), and b to the second step (16.95b); c'_M is the concentration of the intermediate product at an overpotential η. Solving these two equations simultaneously and eliminating the ratio c'_M/c_M, one arrives at the following expression

$$i = 2\frac{e^{-(\alpha_a+\alpha_b)F\eta/RT} - e^{(2-\alpha_a-\alpha_b)F\eta/RT}}{\frac{1}{i_b^0}e^{(1-\alpha_a)F\eta/RT} + \frac{1}{i_a^0}e^{-\alpha_b F\eta/RT}} \tag{16.96}$$

It follows from Eq. (16.96) that when $\eta \ll 0$ (cathodic polarization)

$$i = 2i_a^0 e^{-\alpha_a F\eta/RT} \tag{16.97}$$

and when $\eta \gg 0$ (anodic polarization)

$$i = 2i_b^0 e^{(1-\alpha_b)F\eta/RT} \tag{16.98}$$

It should be noted that for the same overall electrode reaction the number of electrons transferred at one time, the sequence of their transfer and also the retardation at each of these steps may change, depending on the electrolysis conditions, and primarily on the value of overpotential (current density). For example, according to Losev and coworkers the anodic dissolution of copper in the region of low polarizations takes the form of a two-step electrochemical reaction with the loss of one electron at each step

$$[\mathrm{Cu}] = \mathrm{Cu}^+ + e_{[M]}$$
$$\mathrm{Cu}^+ = \mathrm{Cu}^{2+} + e_{[M]}$$

the detachment of the second electron being the slowest step. At high anodic polarizations the dissolution of copper occurs in one step with the simultaneous loss of two electrons.

16.7. THE BASIC KINETIC CHARACTERISTICS OF THE ELECTROCHEMICAL STEP

16.7.1. EXCHANGE CURRENT AND TRANSFER COEFFICIENT

An analysis of kinetic equations describing the phenomenon of electrochemical overpotential shows that its most important characteristics are the *exchange current* i^0 and the *transfer coefficient* α. For the same deviation of the electrode potential from the equilibrium value the reaction rate (the net current density) will be the higher the greater the exchange current density. The latter depends in turn on the nature of the electrochemical reaction, the electrode material and the solution composition. The transfer coefficient

characterizes the effect of the electrical field of an electron on the activation energy of the electrochemical step and also determines the symmetry of the cathodic and anodic processes. It depends relatively little on the electrode material; usually α is close to 0.5.

The values of i^0 and α for a single-step electrochemical act can be found graphically (Fig. 16.2), by plotting η against $\log i$ in that

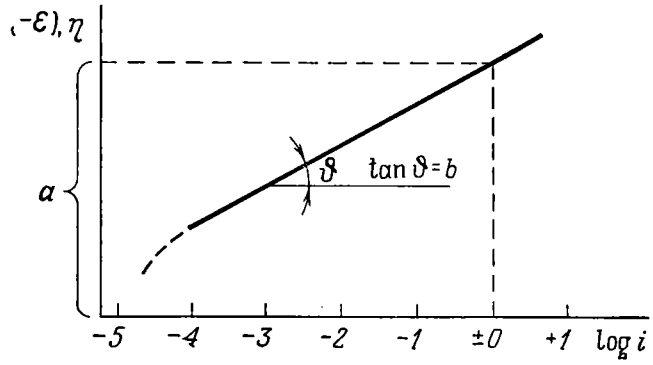

Fig. 16.2. Determining Tafel constants a and b from a semilogarithmic plot of overpotential η against current density i at $\eta \ll 0$ or $\eta \gg 0$ and $\zeta = 0$

region of overpotentials ($\alpha zF\eta \gg RT$) where either Eq. (16.30) (strong cathodic polarization) or Eq. (16.35) (strong anodic polarization) is satisfied. The slope b of the η vs. $\log i$ straight line in Fig. 16.2 is equal to $2.3\,RT/\alpha zF$ and hence

$$\alpha = 2.3\frac{RT}{zFb}$$

The exchange current i^0 can be determined from the value of overpotential a at $\log i = 0$, i.e., at unit current density

$$i^0 = 10^{-a\alpha zF/2.3RT} = 10^{-a/b} \qquad (16.100)$$

Since Eqs. (16.30) and (16.35) lose their meaning at small current densities, it is expedient to utilize for the same purpose the more general expression (16.21) rewritten as follows

$$\ln\frac{i}{1-e^{zF\eta/RT}} = \ln i^0\frac{\alpha zF\eta}{RT} \qquad (16.101)$$

If the experimental data (η_c and i_a taken as negative and η_a and i_c as positive) are presented in the $\ln i/(1 - e^{zF\eta/RT})$ versus η coordinates, as shown in Fig. 16.3, then the slope of the straight line will be equal to $\alpha zF/RT$, and thus we can determine the transfer coefficient α, and the ordinate of the point where $\eta = 0$ will yield the value of $\ln i^0$.

In the case of a two-step electrochemical act the transfer coefficients α_a and α_b and the exchange currents i_a^0 and i_b^0 can be found

from the limiting equations (16.97) and (16.98) rewritten in the form

$$\eta = \frac{RT}{\alpha_a F} \ln 2i_a^0 - \frac{RT}{\alpha_a F} \ln i \qquad (16.102)$$

and

$$\eta = -\frac{RT}{(1-\alpha_b)} \ln 2i_b^0 + \frac{RT}{(1-\alpha_b)} \ln i \qquad (16.103)$$

The graphical construction of the experimental data in the η versus $\ln i$ coordinates for the cathodic and anodic polarizations allows one

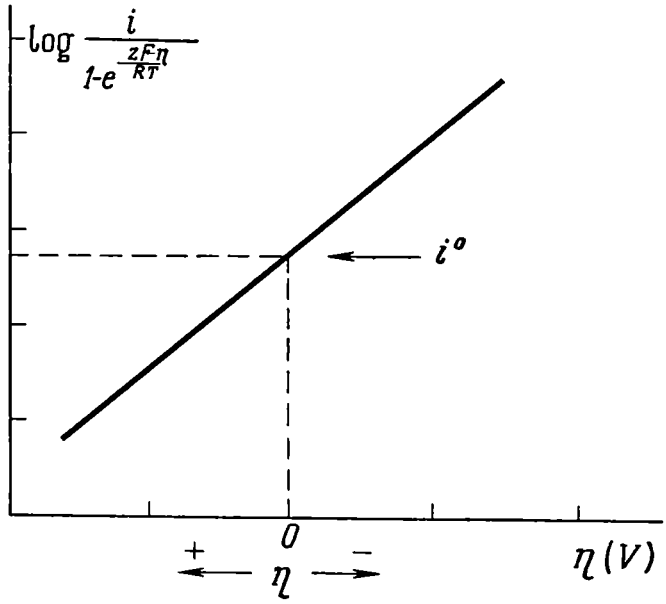

Fig. 16.3. Graphical determination of the exchange current density i^0 and transfer coefficient α by substituting experimental data into Eq. (16.101)

to determine α_a and α_b from the slopes of the straight lines, and the exchange currents i_a^0 and i_b^0 from the values of cathodic and anodic polarizations at $i = 1\text{A/cm}^2$.

If the dependence of the exchange current on the concentration of the participants of the electrode reaction is known, the transfer coefficient can easily be determined by using Eq. (16.18):

$$i^0 = i_{st}^0 c_{\text{Ox}}^{(1-\alpha)} c_{\text{R}}^{\alpha}$$

or, after taking logarithms,

$$\ln i^0 = \ln i_{st}^0 + (1 - \alpha) \ln c_{\text{Ox}} + \alpha \ln c_{\text{R}}$$

The slope of the $\ln i^0$ vs. $\ln c_{\text{Ox}}$ line at constant c_{R} is equal to $1 - \alpha$:

$$\left(\frac{\partial \ln i_0}{\partial \ln c_{\text{Ox}}}\right)_{c_{\text{R}}} = 1 - \alpha \qquad (16.104)$$

and the slope of the $\ln i^0$ vs. $\ln c_R$ line at constant c_{Ox} is equal to α:

$$\left(\frac{\partial \ln i^0}{\partial \ln c_R}\right)_{c_{Ox}} = \alpha \tag{16.105}$$

The relationship between the exchange currents and the activity of the reactants involved was first examined by Esin (1940).

These procedures for finding the basic kinetic characteristics of the electrochemical act yield correct results only when the ζ potential and its variation with overpotential may be ignored, i.e., when the conditions formulated at the beginning of this chapter (see p. 362) are fulfilled. Otherwise, the electrochemical overpotential is described by Eq. (16.67):

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT}\left(\vec{k}c_{Ox}e^{-\alpha zF\varepsilon/RT} - \overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT}\right)$$

or by Eq. (16.68)

$$i = \vec{i} - \overleftarrow{i} = i^0 e^{(\alpha z - z_1)F\zeta/RT}\left(e^{-\alpha zF\eta/RT} - e^{(1-\alpha)zF\eta/RT}\right)$$

In this case the construction of Tafel's relations or relations of the type (16.101) will yield only the apparent value of transfer coefficient since the ζ potential is a function of η. To determine the true value of α one can utilize Eq. (16.68) by rewriting it in the form

$$i\frac{e^{z_1F\zeta/RT}}{1-e^{zF\eta/RT}} = i^0 e^{(\alpha zF/RT)(\zeta-\eta)} \tag{16.106}$$

or, after taking logarithms,

$$\ln i\frac{e^{z_1F\zeta/RT}}{1-e^{zF\eta/RT}} = \ln i^0 + \frac{\alpha zF}{RT}(\zeta-\eta) \tag{16.107}$$

If the left-hand side of Eq. (16.107) is plotted against $(\zeta - \eta)$ or $(\zeta - \varepsilon)$, the slope of the resulting straight line will be equal to $\alpha zF/RT$, making it possible to find the value of α. For the cathodic region Eq. (16.106) simplifies to

$$ie^{z_1F\zeta/RT} = i^0 e^{(\alpha zF/RT)(\zeta-\eta)} \tag{16.108}$$

and for the anodic region it takes the form

$$ie^{(F/RT)(z_1\zeta - z\eta)} = i^0 e^{(\alpha zF/RT)(\zeta-\eta)} \tag{16.109}$$

The true value of transfer coefficient can also be determined by using the last two equations. This method of plotting polarization curves and determining the values of α and i^0 was proposed by Delahay and coworkers; it has been checked on a number of electrochemical reactions. The method presupposes the possibility of calculating ζ [which is identified with the potential drop in the OHP (outer Helmholtz plane) referred to the potential in the bulk of the solu-

tion, which is taken as zero] on the basis of the double-layer theory by using data pertaining to equilibrium conditions. It is assumed that the passage of a current does not essentially affect the double-layer structure. In Delahay's opinion this assumption is sufficiently accurate up to very high current densities.

16.7.2. THE ORDER OF ELECTROCHEMICAL REACTIONS. STOICHIOMETRIC NUMBERS

Other two important characteristics of electrochemical reactions are their order and stoichiometric number. The order of an electrochemical reaction, ν_j, has here the same physical meaning as in the kinetics of chemical reactions, though in this case, apart from the usual parameters—temperature and pressure, ν_j is also a function of electrode potential. The order of an electrochemical reaction in respect to any species of particles, ν_j, can be found by studying the dependence of the current density on the concentration of a given species provided the concentration of all other species, temperature, pressure and electrode potential are constant:

$$\left(\frac{\partial i}{\partial c_j}\right)_{c',\, T,\, P,\, \varepsilon} = \nu_j \qquad (16.110)$$

Equation (16.110) is a direct consequence of general kinetic equations, the differentiation of which with respect to the concentration of the given species yields the order of the cathodic or anodic reaction for this species.

The use of the order of an electrochemical reaction to solve one of the key problems of electrode kinetics—the establishment of the path of a given reaction—can be illustrated by the reduction of iodine to iodide ions.

In a solution containing iodide ions I^- and iodine molecules I_2 complex anions I_3^- are formed, which are reduced in accordance with the overall equation

$$I_3^- + 2e = 3I^- \qquad (16.111)$$

If the reaction proceeded according to the scheme (16.111), the kinetic equation would have the form

$$i = 2F\left(\vec{k}c_{I_3^-}e^{\alpha 2F\varepsilon/RT} - \overleftarrow{k}c_{I^-}^3 e^{(1-\alpha)2F\varepsilon/RT}\right) \qquad (16.112)$$

The order of the cathodic reaction in this case would be as follows:

(1) with respect to I_3^- particles

$$\left(\frac{\partial i}{\partial c_{I_3^-}}\right)_{c',\, T,\, P,\, \varepsilon} = \nu_{I_3^-(c)} = 1$$

(2) with respect to iodide ions I^-

$$\left(\frac{\partial i}{\partial c_{I^-}}\right)_{c',\,T,\,P,\,\varepsilon} = \nu_{I^-(c)} = 0$$

(3) with respect to I_2 molecules

$$\left(\frac{\partial i}{\partial c_{I_2}}\right)_{c',\,T,\,P,\,\varepsilon} = \nu_{I_2(c)} = 0$$

For the anodic reaction one would have accordingly:

$$\nu_{I_3^-(a} = 0; \quad \nu_{I^-(a)} = 3; \quad \nu_{I_2(a)} = 0$$

Experiments have shown however that the order of the cathodic reaction is

$$\nu_{I_3^-(c)} = \frac{1}{2}; \quad \nu_{I^-(c)} = -\frac{1}{2}; \quad \nu_{I_2(c)} = 0$$

and that of the anodic reaction

$$\nu_{I_3^-(a)} = 0; \quad \nu_{I^-(a)} = 1; \quad \nu_{I_2(a)} = 0$$

The scheme of reduction of iodine to iodide that corresponds to experimental reaction orders may be made up of the following steps:

1. $I_3^- = I_2 + I^-$
2. $I_2 = I + I$
3. $2(I + e = I^-)$

The slow step is step 3. It is described by the kinetic equation

$$i = 2F(\vec{k}_3 c_I e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}_3 c_{I^-} e^{(1-\alpha)F\varepsilon/RT})$$

But, according to the equation for step 2

$$K_2 = \frac{c_I^2}{c_{I_2}} \quad \text{and} \quad c_I = (k_2 c_{I_2})^{1/2}$$

and according to the equation for step 1

$$K_1 = \frac{c_{I_2} c_{I^-}}{c_{I_3^-}} \quad \text{and} \quad c_{I_2} = K \frac{c_{I_3^-}}{c_{I^-}}$$

and, consequently,

$$c_I = (K_1 K_2)^{1/2} c_{I_3^-}^{1/2} c_I^{-1/2}$$

from which

$$i = 2F\,[\vec{k}_3\,(K_1 K_2)^{1/2} c_{I_3^-}^{1/2} c_I^{1/2} e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}_3 c_I e^{(1-\alpha)F\varepsilon/RT}] \qquad (16.113)$$

in conformity with experimental data.

The stoichiometric number, ν_s, as defined by Horuiti (1939) indicates how many times the elementary act, which determines the rate of the overall electrode reaction, must occur for the end product to be formed. Thus, if the net charge transferred during the electrode reaction is equal to z, then a charge equal to z/ν_s will be transferred in a once-occurring rds (rate-determining step). For small deviations from equilibrium, at any step, the forward and reverse course of which is associated with an exponential factor containing the activation energy, an equation similar to Eq. (16.24) is valid:

$$i = -i^0 \frac{zF\eta}{RT}$$

If the stoichiometric number is ν_s, Eq. (16.24) should be rewritten in the form

$$i = -i^0 \frac{z}{\nu_s} \cdot \frac{F\eta}{RT} \tag{16.114}$$

or, after solving for ν_s,

$$\nu_s = -i^0 \frac{zF}{RT} \cdot \frac{\eta}{i} = -i^0 \frac{zF}{RT} \left(\frac{\partial \eta}{\partial i}\right)_{\eta \to 0} \tag{16.115}$$

To determine the stoichiometric number from Eq. (16.115) it is necessary to measure overpotentials near the equilibrium potential of a given reaction. As pointed out by Parsons (1955), the stoichiometric number can also be found by using the equation

$$\frac{z}{\nu_s} = b^0 \left(\frac{1}{b_a} - \frac{1}{b_c}\right) \tag{16.116}$$

where $b^0 = 2.3\ RT/F$ and b_a and b_c are the slopes of Tafel straight lines for the anodic and cathodic directions of the reaction.

16.8. THE POSSIBILITY OF PARTICIPATION OF SOLVATED ELECTRONS IN AN ELECTROCHEMICAL ACT

The equations describing the electrochemical overpotential have been derived under the assumption that the elementary electrochemical act involves metal electrons $e_{[M]}$. It would therefore be more correct to write the model equation

$$\mathrm{Ox} + ze = \mathrm{R}$$

in the form

$$\mathrm{Ox} + ze_{[M]} = \mathrm{R} \tag{16.117}$$

Another mechanism is also possible in principle, according to which the first step is the formation of a solvated electron:

$$e_{[M]} + \mathrm{L} = e_s \tag{16.118}$$

and the reduction reaction is a secondary process taking place with participation of solvated electrons e_s:

$$\mathrm{Ox} + ze_s = \mathrm{R} + \mathrm{L} \qquad (16.119)$$

The possible participation of solvated electrons in electrochemical reactions was first indicated by Antropov in 1966 and also by Walker and Hills and Kinnibrugh.

The existence of solvated electrons is not questioned any longer. They are very stable in liquid ammonia but much less stable in amines, alcohols, and in aqueous solutions. Their role in electrode kinetics and also in corrosion phenomena remains still obscure and is the subject of discussion. Some questions associated with the behaviour of solvated electrons in electrochemical processes will be dwelled upon further in connection with the kinetics of concrete electrode reactions.

CHAPTER 17

Some Methods of Investigating Electrode Kinetics

17.1. THE POLARIZATION CURVE METHOD

An exposition, even a brief one, of all methods employed at present for studying the kinetics of electrode processes is outside the scope of a textbook on theoretical electrochemistry. This is rather the concern of books on instrumental electrochemistry (the reader is referred to the literature at the end of the book). Here we will only present the minimum information without the knowledge of which certain problems of theoretical electrochemistry may not be understood.

The basic method of investigating the kinetics of electrochemical reactions is the plotting of curves relating electrode potential to current density. Such curves are usually called *current-potential* or *polarization curves.* Analysis of the shape of polarization curves and study of their dependence on the solution composition, temperature and other physicochemical parameters enables one to obtain sufficiently detailed information about the nature of a particular electrode process. Polarization curves are most frequently plotted by the *direct compensation method.* In this method, a constant current is applied to the electrode under study (the so-called *working* or *test electrode*), and the stationary or steady-state potential is measured (more precisely, the potential difference between the test and reference electrodes). In these measurements (Fig. 17.1) the ohmic voltage drop at the contact (${}_c\varepsilon_{ohm}$), in the current-supplying conductor (up to the point where the compensation and polarizing circuits separate, ${}_1\varepsilon_{ohm}$), in the electrode itself (${}_2\varepsilon_{ohm}$), and in the electrolyte layer between the electrode and the Luggin capillary tip (${}_3\varepsilon_{ohm}$) is included in the measured potential.

The ohmic voltage drop in metallic conductors is usually small and can be either reduced to the desired value (by increasing the cross section of the conductor, reducing its length, etc.) or found by direct measurements and calculations and taken into account. The voltage drop in the electrolyte (due to the resistance of the solution) is more difficult to take into account and it may constitute a noticeable fraction of the value being measured. Kabanov proposed formulas which can be used to calculate the approximate magnitude of the ohmic voltage drop, provided the geometry of the electrode, the method of setting up the Luggin capillary, and the specific

conductivity of the solution are known. Owing to the finite rate of ion transport the electrolyte layer in the immediate vicinity of the electrode has a composition different from that of the original solution. Besides, it changes with current density. All this and also the uncertainty of the specific conductivity value makes calculations difficult. It is therefore recommended that the distance between the Luggin tip and the test electrode be minimized, thereby reducing the possible ohmic drop in the solution. It should be remembered, however, that part of the electrode surface may be shielded by the

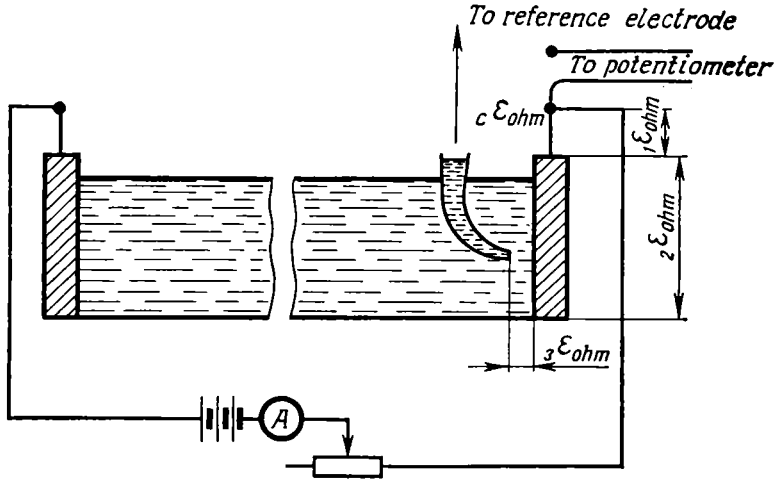

Fig. 17.1. Schematic representation of possible ohmic potential drops included in the electrode potential measured by the direct compensation method

Luggin capillary tip. The current density on the portion of the electrode surface under the capillary tip may be lower than its mean value on the electrode, and this will distort the results of measurement. This undesirable effect can be avoided or, at least, reduced to a minimum by using special types of Luggin capillaries. Even when all the necessary precautions are taken, the ohmic potential drop will still be included in the value measured by the direct compensation method after a poorly conducting layer consisting of reaction products is formed on the electrode surface.

It was once thought that the deviation of the potential under an applied current was always caused by the potential drop in a certain hypothetical transition layer. The desire to check the validity of this assumption led to the development of an *indirect* or *commutator method*, in which the electrode potential is measured a short time after the interruption of the polarizing current. The results of the measurements carried out by Newberry in 1914-16, who used the commutator method, were in sharp discord with those obtained by the direct compensation method under similar conditions. The polarization values were found to be lower, as a rule, and even the

character of the current-potential dependence was different sometimes. The use of electronic circuits in the commutator method has made it possible to reduce the time interval between the interruption of the current and the measurement of potential and to carry out measurements at different times after the interruption. If data obtained at different times are extrapolated to $t = 0$, as was done, for example, by Glasstone (1924) and Hickling (1941), then both methods yield consistent results within the experimental error. It has thus been proved that both the direct and the commutator method can be used to plot polarization curves. The coincidence of the results provided by the two methods indicates also that there is not any special intermediate resistance and that polarization phenomena are kinetic in nature.

The existence of an ohmic voltage drop which causes, like any type of polarization, a deviation of the electrode potential from the equilibrium or stationary (open-circuit) value, led to the introduction of the concept of *ohmic* or *resistance polarization*. This quantity however is not associated, with a few exceptions (such as the change of the composition near the electrode due to concentration polarization), with the kinetics of electrode processes and should not therefore be regarded as a special type of overpotential.

In tracing polarization curves, fluctuations of the potential with time are observed, which occasionally result in a spontaneous change of the applied current. Such fluctuations of potential and current are especially noticeable in the region of limiting currents. Therefore, apart from ordinary methods of obtaining current-potential curves, ever increasing use is made of the so-called *potentiostatic* and *galvanostatic methods*. In the first method, the potential of the test electrode is adjusted to a specified value, which can be kept constant for a long time by means of a special electric circuit. The current corresponding to the given potential is registered up to the moment when the constant potential is set up. A series of such measurements yields a *potentiostatic i vs. ε curve*. In the galvanostatic method, the current is kept constant and the variation of the potential is measured as a function of time until it attains a constant value. The relation between i and ε obtained is called the *galvanostatic curve*. The combined use of these methods enables a more detailed study of the behaviour of electrochemical systems.

17.2. OTHER METHODS OF INVESTIGATION

When a current is applied to a cell and also when it is reduced or increased, the corresponding electrochemical changes occur not instantaneously but at a finite rate. A study of the process of establishment of the potential in time (potential-time curves) on application of a current (charging curves) or after switching off the current (cur-

rent-decay curves) may provide additional information on the kinetics of electrode reactions. For the same purpose curves are plotted which show the variation of current with time (I versus t) at different potentials. Of greater importance in this connection are methods using current pulses.

When no electrochemical reaction takes place at the electrode-electrolyte interface, the whole quantity of electricity passed is spent on charging the double layer, resulting in a corresponding change in the potential. An electrical analogue of such an electrode, which was defined earlier as ideally polarizable, is a parallel-plate condenser. Because of the electrochemical reaction not all the quantity of electricity is expended on charging the double layer; part of it passes through the electrode-electrolyte interface. Here a circuit consisting of a capacity and a parallel-connected resistance may be taken as an electrical analogue. The capacity of the condenser corresponds to that of the electric double layer, and the resistance (under certain conditions) may be regarded as the inverse of the rate of an electrochemical reaction. A study of the dependence of the capacity of the double layer and its electrical resistance on potential with the aid of suitable alternating-current circuits is another effective method of investigating the kinetics of electrochemical reactions. This method was developed by Dolin, Frumkin and Ershler (1940). From data on the double-layer capacity inferences can be drawn as to the state of the electrode surface and the nature of the adsorption of various substances on the electrode.

Still another effective method was developed by Levich et al. It is based on the use of a rotating-disc electrode and enables one to determine the role of transport, discharge and chemical transformation steps in the overall electrode reaction.

Frumkin and Nekrasov proposed a combination of a disc electrode and a ring electrode enclosing it. The electrodes are mechanically connected, forming an assembly, which is rotated about its axis. But they are isolated electrically. Owing to this construction the electrodes can be polarized independently from an external current source so that one electrode becomes the anode and the other the cathode. The tracing of a polarization curve for the ring electrode permits one to identify qualitatively the reaction products formed on the disc electrode. This method has made it possible, for example, to investigate the reduction of oxygen and to determine the amount of hydrogen peroxide formed in this process.

As shown by the equations of the slow-discharge theory, the basic parameters determining the kinetics of an electrochemical reaction are the transfer coefficient α and the exchange current I^0. Determination of these parameters is therefore very important. In this connection mention should be made of a method for calculating α and I^0 based on the *redox-kinetic effect.*

The redox-kinetic effect (known as *faradaic rectification*) was discovered by Doss, an Indian scientist, in 1950 and later subjected to a detailed study by Doss and his coworkers and also by other scientists. This effect consists in the following. When an alternating current is applied to the electrode, the latter's potential is shifted by a certain amount one way or the other. This departure of the electrode potential is called the *redox-kinetic potential* ψ. The relation between the redox-kinetic potential ψ and the kinetic parameters α and I^0 can be derived, to a certain approximation, from Eq. (16.21). If an alternating current is imposed on an electrode which is in equilibrium with the corresponding ions in solution, the electrode will be polarized cathodically during the cathodic half-period; the relation between $\vec{\eta}$ and $\vec{i}$ (provided that the rds is the discharge step) will be expressed through Eq. (16.30):

$$\vec{\eta} = -\frac{RT}{\alpha z F} \ln \frac{\vec{i}}{i^0}$$

Similarly, for the anodic half-period one has according to Eq. (16.35):

$$\overleftarrow{\eta} = \frac{RT}{(1-\alpha) z F} \ln \frac{\overleftarrow{i}}{i^0}$$

When the potential is shifted sufficiently far away from equilibrium,

$$|\vec{i}| - |\overleftarrow{i}| = |i|$$

and the difference $|\vec{\eta}| - |\overleftarrow{\eta}|$ corresponds, by definition, to the redox-kinetic potential, i.e.,

$$\psi = |\vec{\eta}| - |\overleftarrow{\eta}| = -\frac{RT}{zF}\left(\frac{1}{\alpha} - \frac{1}{1-\alpha}\right) \ln \frac{|i|}{i^0} \qquad (17.1)$$

From the last expression it follows that if $\alpha = 0.5$, then $\Psi = 0$. If α is different from 0.5, the value of Ψ is no longer equal to zero, and the more α departs from 0.5, the higher will be the absolute value of the redox-kinetic potential. If the value of α is determined by another method, the redox-kinetic potential can be used for evaluating the exchange current.

The faradaic rectification effect lies at the basis of one of the modification of the polarographic method of analysis (radiowave polarography).

The kinetics of electrochemical processes is studied not only by electrical methods. For example, radioactive isotopes are used to determine exchange currents and to investigate the adsorption on electrodes. A number of methods have been devised and applied in studying the kinetics of particular electrochemical reactions. For instance, thin metal membranes are used to study the diffusion of electrolytically formed hydrogen into the bulk of the electrode

and to establish the relation between this process and the transfer of the potential to the non-polarizable side of the membrane. By studying the temperature dependence of the rate of electrochemical reactions one can understand better the nature of these reactions. The rate constant of a chemical reaction, i.e., the reaction rate at unit concentrations of reactants is related to temperature by the Arrhenius equation:

$$\ln k = B - \frac{u}{RT} \tag{17.2}$$

where u = energy of activation
B = a temperature-invariant constant depending on the reaction type.

The temperature coefficient of the rate constant

$$\frac{d \ln k}{dT} = \frac{u}{RT^2} \tag{17.3}$$

is thus determined by the energy of activation.

For electrochemical reactions the rate constant k may be replaced by an equivalent quantity—the current I or current density i. A mere substitution of the current I for the rate constant however does not yet render Eq. (17.3) applicable to electrochemical reactions because the activation energy of these reactions is dependent on the electrode potential (Temkin, 1948). With changing electrode potential the activation energy of the same electrochemical reaction at given concentrations of reacting substances may vary within wide limits. Therefore, a comparison of the rates of an electrochemical reaction at different temperatures makes sense only when the electrode potential remains constant. Thus, for electrochemical reactions Eq. (17.3) should be rewritten in the form:

$$\left(\frac{\partial \ln i}{\partial T}\right)_{\varepsilon} = \frac{u_{\varepsilon}}{RT^2} \tag{17.4}$$

where u_{ε} is the energy of activation at a given potential ε. Since the condition for the constancy of the electrode potential at different temperatures is unfeasible, measurements are carried out with the overpotential η being kept constant:

$$\left(\frac{\partial \ln i}{\partial T}\right)_{\eta} = \frac{u_{\eta}}{RT^2} \tag{17.5}$$

Equation (17.2) rewritten for electrochemical reactions has the form

$$\ln i_{\eta} = B - \frac{u_{\eta}}{RT} \tag{17.6}$$

In contrast to the activation energy u_ε at constant potential, the activation energy u_η at constant overpotential is called the *effective activation energy*.

The applicability of Eqs. (17.5) and (17.6) to electrochemical reactions was proved by Gorbachev and coworkers (1950). They showed that on the basis of the activation energy u_η and its dependence on polarization η one can draw inferences as to the nature of polarization. For example, if the activation energy is close to 3 kcal/mole and is almost independent of overpotential, the appearance of an overpotential should most probably be ascribed to the slow occurrence of diffusion. Conversely, if the activation energy is high (about 10 kcal/mole or higher) and decreases noticeably with overpotential, this is indicative of the chemical nature of the overpotential. The Gorbachev method of studying kinetically electrochemical processes, which is based on the determination of the activation energy and its dependence on various factors, is termed the *temperature-kinetic method.* This method finds ever increasing use for investigating the kinetics of the electrodeposition and electrodissolution of metals.

17.3. PREPARATION OF SOLUTIONS AND ELECTRODES FOR ELECTROCHEMICAL STUDIES

The high response of the electrode potential during the passage of a current to changes in the solution composition, particularly to the presence even of negligible amounts of surface-active substances and catalytic poisons calls for special care in preparing solutions and electrodes for studies of electrochemical kinetics. This circumstance was overlooked in early works and many old data on chemical polarization cannot therefore be trusted.

A procedure for hydrogen evolution on mercury providing reliable polarization data was developed by Frumkin's school (1937). It involves removal of gases from solutions, preliminary electrolysis of the latter and also special preparation of the electrode surface. The purity of solutions is important not only in the cathodic evolution of hydrogen but also in the electrodeposition of metals. Purity requirements in electrodeposition of metals which ensure obtaining reliable data were recommended by Vagramyan. A special procedure for preparing solutions and electrodes was employed by Antropov and Mizgireva in studying the kinetics of the electrochemical reduction and oxidation of inorganic and organic substances. Later Bockris formulated some general rules for making solutions of required purity.

CHAPTER 18
Polarography

Kinetic regularities specific for electrochemical reactions constitute the basis of one of the most perfect and universal methods of research and chemical analysis called the *polarographic method* or *polarography*. The name polarography reflects its close relation to polarization phenomena observed in electrolysis. This technique was introduced by the Czechoslovak electrochemist Jaroslav Heyrovsky[1)] in 1922. Three years later Heyrovsky and Schicata designed an apparatus, known as the *polarograph*, for automatic polarographic analysis.

The polarographic method proved to be so promising and interesting that it left behind older electrochemical methods such as conductometry, potentiometry and electroanalysis.

18.1. CLASSICAL POLAROGRAPHY

The chemical analysis of a solution in polarography is carried out with the aid of current-potential curves. These curves are traced by using a special cell including a dropping-mercury electrode and any practically non-polarizable electrode, most frequently mercury. The latter is placed at the bottom of the cell; it has a large surface area as compared with the mercury drop. Since the current flowing through the polarographic cell is small (about 10^{-6} A) and the cell resistance is low, the ohmic potential drop is negligible. The current density at the macroelectrode is also small owing to the large surface area and causes no perceptible change in the electrode potential. At the same time the surface area of the drop does not exceed 0.1 cm^2 and therefore the current density here is hundreds of times higher and may cause its potential to deviate considerably from the equilibrium value. In fact, the buildup (or drop) of the voltage across the polarographic cell with current should be wholly ascribed to the change in the potential of the dropping-mercury electrode.

The polarographic setup is shown schematically in Fig. 18.1. In polarographic experiments, the potential applied across the cell

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[1)] J. Heyrovsky was awarded the Nobel prize in 1959 for this contribution to electrochemical methods.—*Tr.*

is varied and the current is measured as a function of this potential, i.e., *current-potential curves* or curves of current versus the potential of the dropping-mercury electrode are plotted. The potential can be varied by means of a potentiometer and the current is measured with a microammeter (so-called *visual polarography*). For analytical purposes it is more convenient to use automatic polarography: a potential varied in a predetermined manner is continuously applied across the cell and the corresponding variations in the current are automatically recorded either on photographic paper by a light beam from a mirror galvanometer or on ordinary paper by means of a pen recorder.

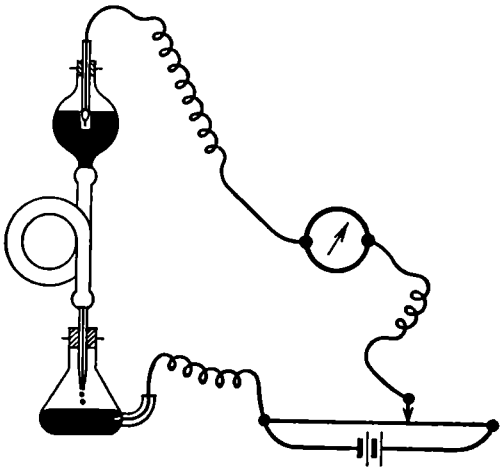

Fig. 18.1. Polarographic setup

If the solution contains only one species of particles capable of undergoing reduction at the mercury electrode at a certain potential, the resulting curve will have the shape shown in Fig. 18.2. If several species of particles reducible at different potentials are present in the solution, a curve of the form shown in Fig. 18.3 is obtained. Such curves are called *polarograms* and a section corresponding to the reduction of a definite species is known as the *polarographic wave* (or *step*).

Qualitative polarographic analysis is based on determination of *half-wave potentials* (the potentials corresponding to inflection points on polarographic waves, where the current is half the limiting current) and on their comparison with the known half-wave potentials of various substances. Quantitative polarographic analysis is based on the measurement of wave heights corresponding to diffusion limiting currents of reduction.

The polarographic wave equation for the reduction of the ions of a metal soluble in mercury can be deduced as follows. According to Eq. (7.57) the equilibrium potential of an amalgam electrode is determined by the ratio of the ionic activity of a metal in the solution to the activity of its atoms in the amalgam:

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_{M^{z+}}}{a_{M(Hg)}}$$

In polarographic measurements, use is made of solutions diluted with respect to the ions being determined and corresponding dilute amalgams are produced at the cathode, and therefore in Eq. (7.57)

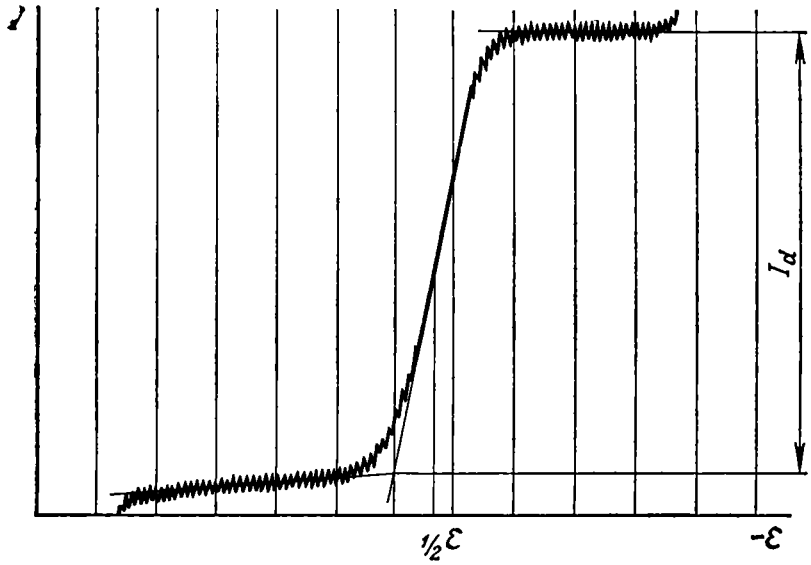

Fig. 18.2. Typical polarographic curve corresponding to the reduction of a single species of particles

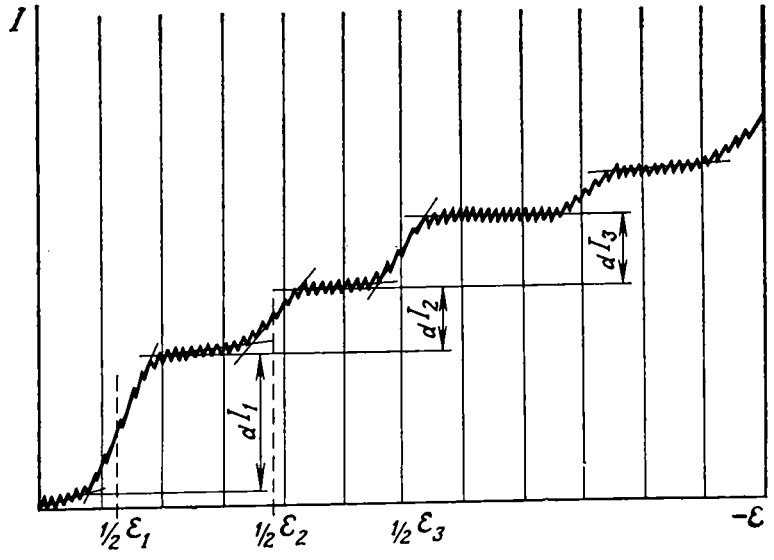

Fig. 18.3. Polarogram

the activities may be replaced by the concentrations:

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{c_{M^{z+}}}{c_{M(Hg)}} \tag{18.1}$$

An amalgam is formed when the metal ions are discharged at the surface of the mercury drop. The concentration of the amalgam must therefore be proportional to the current:

$$c_{M(Hg)} = k'I \tag{18.2}$$

In polarographic analysis, the concentration of a given substance is always determined in a solution containing an excess of an indifferent substance, which is termed the *background* or *supporting electrolyte*. The background electrolyte suppresses the migration of the ions to be determined, these ions being transported to the surface of the mercury drop exclusively by diffusion. Under these conditions the limiting current I_d (the maximum diffusion current) is proportional to the concentration of the reducible substance in the solution:

$$I_d = k''c^0_{M^{z+}} \tag{18.3}$$

and corresponds to complete depletion of the solution in ions to be determined near the drop surface, i.e., $c_{M^{z+}(sur)} = 0$.

At any current I lower than I_d the concentration of metal ions is different from zero and corresponds to the value $c_{M^{z+}}$, which determines, according to Eq. (18.1), the electrode potential. Under these conditions the diffusion current is equal to

$$I = k''(c^0_{M^{z+}} - c_{M^{z+}})$$

Using Eq. (18.3), one can rewrite the last expression in the following form

$$I = I_d - k''c_{M^{z+}}$$

whence

$$c_{M^{z+}} = \frac{1}{k''}(I_d - I) \tag{18.4}$$

Substituting the values of $c_{M(Hg)}$ and $c_{M^{z+}}$ from Eqs. (18.2) and (18.4) into Eq. (18.1), one has

$$\varepsilon = \varepsilon^0 - \frac{RT}{zF} \ln k'k'' - \frac{RT}{zF} \ln \frac{I}{I_d - I} \tag{18.5}$$

If

$$I = \frac{1}{2} I_d$$

then

$$\varepsilon = \varepsilon^{\circ} - \frac{RT}{zF} \ln k'k'' = \varepsilon_{1/2}$$

where $\varepsilon_{1/2}$ is the half-wave potential determined by the nature of discharging ions but not by their concentration. Upon substituting the value of the half-wave potential Eq. (18.5) simplifies to

$$\varepsilon = \varepsilon_{1/2} - \frac{RT}{zF} \ln \frac{I}{I_d - I} \tag{18.6}$$

Equation (18.6), derived by Heyrovsky and Ilkovic in 1935, is the basic equation of the polarographic wave. It is applicable not only to the discharge of the ions of metals soluble in mercury but also to many other electrode processes, particularly reduction-oxidation reactions.

For reactions involving noticeable chemical polarization the slope of the ε vs. ln $(I/I_d - I)$ straight line is usually greater than the quantity RT/zF. This can be taken care of by introducing a factor $1/\alpha$ into Eq. (18.6), it being assumed that $0 < \alpha < 1$.

Equation (18.6) shows that at $I = I_d$ the electrode potential tends to an infinitely large negative value and under these conditions an almost horizontal plateau would be expected to appear on the I vs. ε curve, corresponding to a sharp change in the potential at a small variation of the current (see Fig. 18.2). In reality, the potential is displaced to a value at which the next electrode process is possible and a second, third, etc., polarographic wave may appear (see Fig. 18.3). The quantity I_d, governing the shape of a polarographic wave and related to the concentration of the reducible substance by the expression (18.3), is the so-called *mean diffusion limiting current*. When a dropping-mercury electrode is used, the diffusion current changes periodically because the surface area of the drop grows continuously during its formation from a very small value (at the moment immediately following the release of the previous drop) up to a certain maximum value (at the moment just before the expanding drop falls off). This change of the instantaneous current I'_d during the growth of a mercury drop is shown in Fig. 18.4. The instantaneous current I'_d and the mean current I_d can be calculated by the Ilkovic equations:

$$I'_d = 706zc\Delta^{1/2}m^{2/3}\tau^{1/6} \tag{18.7}$$

and

$$I_d = 606zc\Delta^{1/2}m^{2/3}\tau^{1/6} \tag{18.8}$$

Equations (18.7) and (18.8) determine the instantaneous current I'_d and the mean current I_d in microamperes if the quantities contained in them are expressed in the following units: the Faraday number F in coulombs (this quantity has been included in the numerical

factors); the concentration c of the reducible substance or ion expressed in mmole/litre; the diffusion coefficient Δ in $cm^2 \cdot sec^{-1}$; the rate of mercury flow m in $mg\text{-}sec^{-1}$; the drop-time or the lifetime of a single drop, τ, in seconds.

Equation (18.8) could be used as a basis for calculating the concentration of the unknown substance from the limiting current I_d on the polarogram and the product $m^{2/3}\tau^{1/6}$ previously found for the capillary if the diffusion coefficients Δ were known with sufficient accuracy. The values of diffusion coefficients however cannot

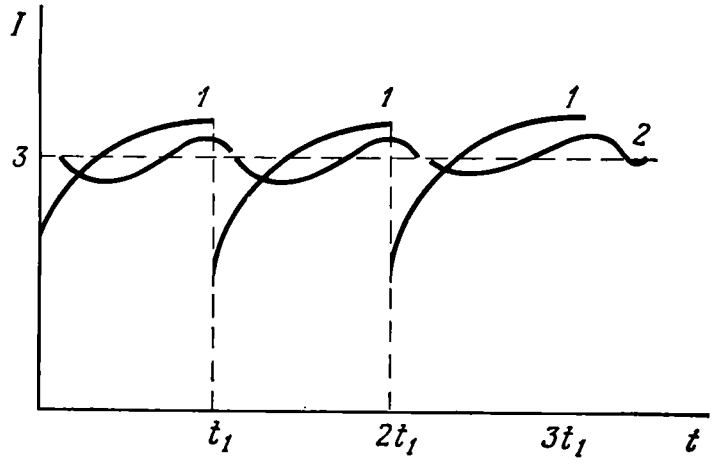

Fig. 18.4. Variation of current during the formation, growth and release of a mercury drop:

t_1—drop-time; *1*—true current; *2*—current measured by galvanometer; *3*—mean current

be considered reliable; besides, they depend on the overall composition of the solution and therefore in quantitative analysis resort is made to special procedures, which are also based on the Ilkovic equation. For example, according to one of the methods polarograms are taken for a series of solutions containing the same amount of the background electrolyte but different amounts of the substance to be analysed. The calibration c vs. I_d curve obtained from these data is then used to determine the concentration c from the measured current I_d. In another variant, a polarogram is prepared for the test solution and I_d is determined, after which a fresh portion of the solution containing a definite amount of the substance to be analysed is introduced into the cell and a new polarogram is taken. The amount of the substance in the original sample is found from the known volume of the solution by comparing the currents. And, finally, where a series of tests of the same substance is to be made, standard solutions containing a known amount of the substance to be analysed are used, and the concentration of this substance in the test sample is found by comparing the limiting currents in the sample and in the standard solution.

The polarographic method is particularly convenient for determining the content of metals in alloys, for analysis of minerals and ores, and for detecting metal impurities in various preparations. It is also used for quantitative determination of many organic substances capable of undergoing reduction or oxidation and of oxygen in technical gases, etc. The error in polarographic analysis of various substances does not exceed 2-5 per cent if their content in the sample ranges from 10^{-2} to 10^{-5} mole/litre. In some cases the sensitivity of the polarographic method is still higher. For example, platinum salts, cysteine, cystine and other organic compounds containing —SH and $-NH_2$ groups can be detected and determined quantitatively even when their concentrations are as low as 10^{-6} to 10^{-7} mole/litre. In the presence of platinum the hydrogen wave starts at more positive potentials and its height increases with platinum concentration in the solution. These effects are probably associated with the fact that the evolution of hydrogen proceeds much more readily on platinum than on mercury. The increased sensitivity of the method in the presence of compounds containing —SH and $-NH_2$ groups should be attributed to their catalytic effect on the process of hydrogen evolution. In this case the hydrogen wave originates at higher than usual positive potentials and has a greater height.

The effect observed in the presence of organic substances is explained on the basis of the Brönsted theory, assuming an equilibrium in solutions of these substances:

$$B + H_3O^+ = BH^+ + H_2O \qquad (18.9)$$

where B is the basic and BH^+ its conjugate acidic form of the organic substance. The acid BH^+ is discharged at the mercury drop to produce an uncharged complex BH:

$$BH^+ + e = BH \qquad (18.10)$$

which then decomposes with liberation of hydrogen and recovery of the original substance:

$$2BH = 2B + H_2 \qquad (18.11)$$

All these reactions proceed at a higher rate than the direct evolution of hydrogen.

Polarography is also employed to investigate various physicochemical phenomena. Polarograms can yield information about the type of reducible ions in solutions, the composition and stability of complexes, the number of electrons participating in the reduction reaction; they are used to study the kinetics of electrochemical transformations and, in particular, to find out the number of steps involved in electrochemical reactions. In all cases where reactions of electroreduction are studied it is advisable to use a dropping-mercury electrode. It is precisely in reduction reactions that the

advantages of the DME are revealed to the full: surface purity owing to the continuously renewed surface of the mercury drop; a wide range of negative potentials due to the high hydrogen overpotential at the mercury cathode, which makes it possible to carry out almost any reduction reaction; high reproducibility of the results obtained, etc. At the same time mercury is not quite suited for studying oxidation reactions and for analysis of anions because of the low oxygen overpotential and the possibility of its oxidation. That is why, apart from dropping-mercury cathodes, solid microelectrodes are also used in polarography. The best material for solid microelectrodes is platinum, which possesses high chemical stability, sufficiently high oxygen overpotential and good mechanical properties. Platinum microelectrodes find use not only in the study of oxidation processes but also in the polarographic analysis of fused salts (Delimarsky). Polarographic analysis with solid microelectrodes is conducted in the same way as with the dropping-mercury electrode. Steady-state diffusion is achieved in this case by using rotating or vibrating electrodes, by stirring the solution, etc. The renewal of the electrode surface and removal of reaction products from it is accomplished either mechanically or through electrochemical dissolution. But even when all these measures are taken, the accuracy and reproducibility inherent in dropping-mercury electrodes cannot be achieved. For this reason polarography with solid cathodes has limited use and is resorted to only in cases where the use of dropping-mercury electrodes is impossible.

Much attention has recently been paid to amalgam polarography in which dilute amalgams of some metals are used instead of mercury. It has a number of advantages over true polarography in studies of diffusion and complex-formation and in determinations of exchange currents. The procedure of amalgam polarography enables the qualitative identification not only of the complex predominating in the solution but also of the complex directly participating in the discharge process (Strömberg).

18.2. AMPEROMETRIC TITRATIONS

The existence of a simple relationship between the concentration of a substance and its polarographic current was used for developing a sensitive and convenient analytical technique called the *amperometric titration* [1]. In this method, the diffusion limiting current serves

[1] The term *amperometric titrations* was introduced by Kolthoff and coworkers (1939). This name is used extensively in polarographic literature. Other terms for this method are also known. For example, Majer (1936) coined the term *polarimetric titrations* since the current passing through the polarized electrode is measured. The name suggested by Lange is *limiting current titrations* because the essential fact here is that the polarizable electrode indicates the limiting current.—*Tr.*

as an indicator. A change in the concentration of the substance to be determined (this substance is transformed in the course of titration into a form incapable of being polarographically reduced) is immediately reflected in the value of the limiting current. By measuring the current (at a constant potential of the dropping-mercury electrode in the region of limiting current) after each addition of the titrant and plotting the limiting current as a function of the volume of reagent added, amperometric curves are obtained.

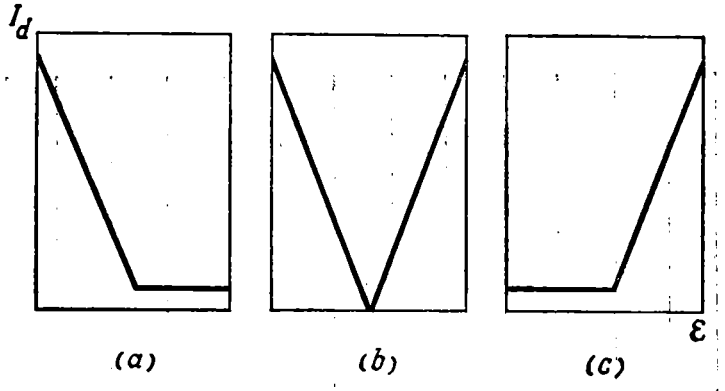

Fig. 18.5. Amperometric titration curves

Some typical curves are shown in Fig. 18.5. Curve *a* corresponds to the case when the substance to be determined is polarographically active and the reagent used in titrations gives no polarographic wave. Curve *b* is obtained when both the substance to be determined and the reagent added are capable of giving a polarographic wave. Curve *c* refers to a polarographically inactive substance titrated by a solution of a reagent giving rise to a diffusion current. Of particular interest is curve *c*, which shows that amperometric titrations can be used to determine substances that do not lend themselves to ordinary polarographic methods. Thus, the possibilities of amperometric titrations are wider from the analytical point of view as compared with true polarography. Moreover, it ensures greater accuracy and permits using solid microelectrodes.

18.3. POLAROGRAPHIC MAXIMA

Polarograms are often more intricate than those shown in Fig. 18.3. If no special precautions are taken, sharply defined peaks or humps, called *polarographic maxima*, may appear on polarograms (Fig. 18.6). The appearance of maxima interferes with analysis by distorting the shape of the wave and hampering the determination of wave heights.

Heyrovsky ascribes the occurrence of maxima to adsorption phenomena. He noticed that there are usually no maxima in the

immediate vicinity of the zero-charge potential and suggested that a distinction be made between *positive* and *negative maxima*, depending on whether they appear on the rising or falling portion of the electrocapillary curve.

The most comprehensive interpretation of the nature of polarographic maxima was based on the conceptions formulated by Frumkin, Bruns, Iofa and their colleagues (1934-39). According to these conceptions, the increase of the diffusion-controlled current above its normal value is caused by additional vigorous stirring of the

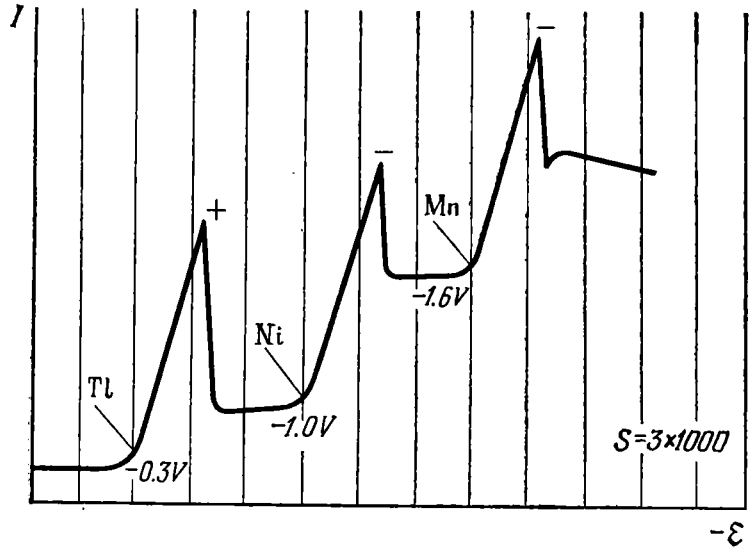

Fig. 18.6. Polarographic maxima in the deposition of thallium, nickel, and manganese

solution near the mercury drop surface. Additional agitation of the solution is in turn caused by internal streaming in the mercury due to nonuniform polarization and the associated difference in the surface tension between different parts of the mercury surface. Streaming in the solution near the mercury drop was confirmed experimentally by Stackelberg and Antweiler (1938) and also by Kryukova and Kabanov (1938). The direction of streaming is different for positive and negative maxima. Streaming occurs from the neck (top) of the drop in the case of positive maxima and in the reverse direction at negative maxima (Fig. 18.7).

The origin of streaming and the occurrence of polarographic maxima can be explained qualitatively as follows. Owing to the screening effect of the capillary the neck of the drop is less strongly polarized than its bottom. Suppose the potential difference between the neck and the bottom of the drop is $\Delta\varepsilon$ (Fig. 18.8). If this potential difference appears on the rising portion of the electrocapillary

curve (which implies the appearance of positive maxima), then to it there will correspond the difference in surface tension $\Delta\sigma$. Since the surface tension at the neck of the drop is lower than at the bottom, the mercury will stream from the neck to the bottom (Fig. 18.7*a*); the adjacent solution layers taken along by this motion flow in the same direction. Fresh solution is thus brought to the neck of the drop, while partially exhausted layers of solution flow to the bottom. This process still further increases the potential difference between the neck and the bottom of the drop, the increase being the greater, the lower the concentration of the solution near the drop, i.e., the more negative its mean potential. Therefore the value of $\Delta\varepsilon$ does not remain constant and increases somewhat: $\Delta\varepsilon < \Delta\varepsilon' < \Delta\varepsilon''$.

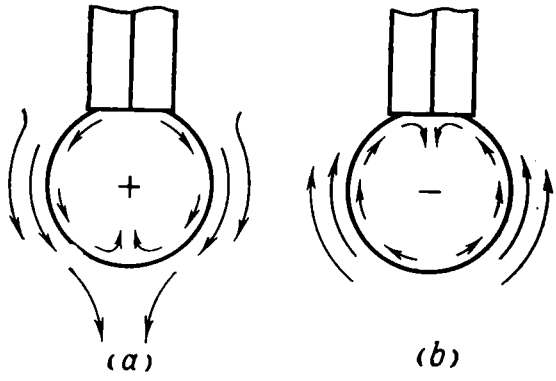

Fig. 18.7. Streaming in a drop and in the adjacent solution layer: *a*—appearance of positive maxima; *b*—appearance of negative maxima

However, in spite of the increase of $\Delta\varepsilon$ due to the shift of the potential to the negative side, the quantity $\Delta\sigma$ (which is directly responsible for the motion) decreases and becomes vanishingly small on approaching the electrocapillary zero and the current drops to its normal value (Fig. 18.8).

When dealing with negative maxima, the electrode potential being on the falling (negative) portion of the electrocapillary curve, the surface tension is lower at the bottom of the drop than that at the neck, which is less negatively charged. The surface at the bottom therefore tends to expand and that at the neck to contract, this causing the mercury to move in the direction indicated in Fig. 18.7*b*. In this case, fresh solution is brought to the bottom of the drop and the solution near the neck is partially exhausted. As a result, the polarization becomes less nonuniform. The levelling effect becomes stronger with decreasing concentration of the solution near the drop, i.e., $\Delta\varepsilon$ decreases as the potential is displaced to the negative side, and this results in a gradual decay of the negative maximum (see Fig. 18.8). Another cause for the disappearance of the negative

maximum is the increase of the charge on the mercury surface with increasing distance from the electrocapillary zero. This must reduce the mobility of the surface layers of mercury and hence the intensity of motion of the solution.

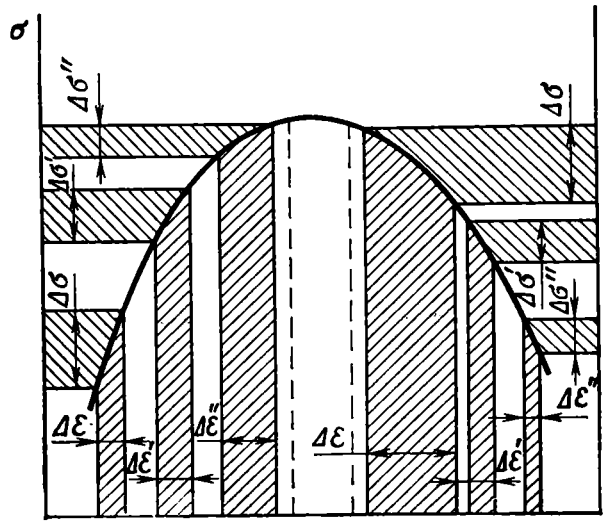

Fig. 18.8. Variation of the potential difference Δε between the neck and the bottom of a mercury drop versus the corresponding difference in surface tension Δσ for different sections of the electrocapillary curve

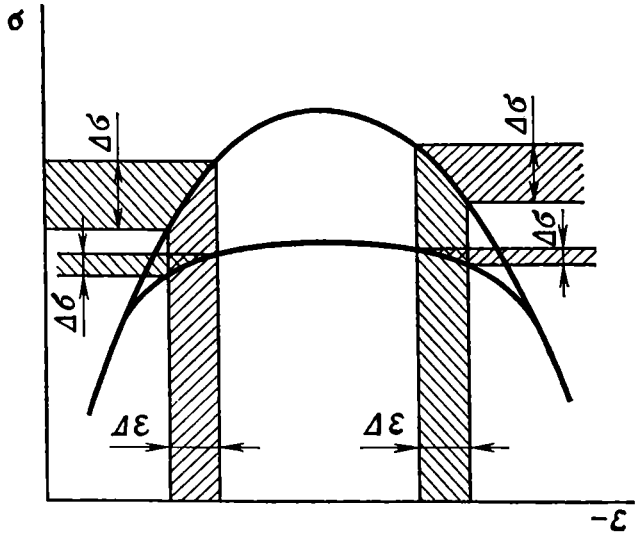

Fig. 18.9. Mechanism of suppression of a polarographic maximum by adding a surface-active molecular substance

To avoid polarographic maxima and obtain normal polarograms, surface-active substances are added to the solution under study. The most effective surface-active substances are those of the molecular type (e.g. gelatine and various dyes). The mechanism of their

action can be explained with the aid of electrocapillary curves (Fig. 18.9). In the presence of such surface-active substances the surface tension remains practically constant over a wide range of potentials. In this case $\Delta\sigma$ is found to be close to zero and cannot provide an intensive tangential motion of the surface layers of the mercury. The ability of a particular surface-active substance to suppress polarographic maxima is linearly dependent on its concentration in the solution. These results were used to develop a sensitive method of quantitative determination of surface-active substances, thereby extending the range of applicability of polarography. This further enhanced the interest in the study of polarographic maxima.

The occurrence of tangential motions of a liquid cathode at nonuniform polarization plays an important role not only in pola rographic practice but also in preparative and industrial electrochemistry. This phenomenon has served as a basis for designing original laboratory electrolytic cells, which intensify the process of electrosynthesis and automatically remove the products from the reaction zone (Starostenko). It has also been shown that the intensity of tangential motions may sharply increase when dilute amalgams are formed and the heterogeneity of the composition of the liquid electrode is superposed on its polarization nonuniformity (Antropov). This intensified tangential motion affects considerably the conditions of electrolysis of chloride or alkali solutions with amalgam electrodes (Chviruk).

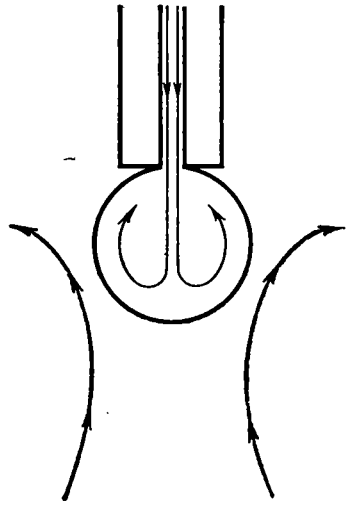

Fig. 18.10. Streaming inside a drop during its formation

In the absence of nonuniform polarization the formation of a mercury drop may itself give rise to streaming in its surface layer (Fig. 18.10). This streaming may entrain the solution layer adjacent to the drop and increase the limiting current. The increase of the current observed in this case was examined by Kryukova (1940), who suggested that this current increase be named a *maximum of the second kind*. In contrast to maxima of the first kind, maxima of the second kind occur most distinctly in the region of potentials adjacent to the electrocapillary zero. The charge in this region is small and does not interfere with the motion of the mercury surface layers.

The existence of maxima of the second kind has been utilized in developing the polarographic adsorption method of analysis. These maxima ensure a better reproducibility of results and higher sensitivity of the method than maxima of the first kind. For example, the presence of *n*-octyl alcohol in the solution (up to 6×10^{-6} mole/lit-

re) does not affect the height of maxima of the first kind observed in the reduction of oxygen. At the same time the height of the oxygen maximum of the second kind decreases by half if the solution contains only 3×10^{-6} mole/litre of this alcohol.

It has recently been found that adsorption phenomena can be studied quantitatively not only by using polarograms and maxima appearing on them but simply by measuring the current on a single

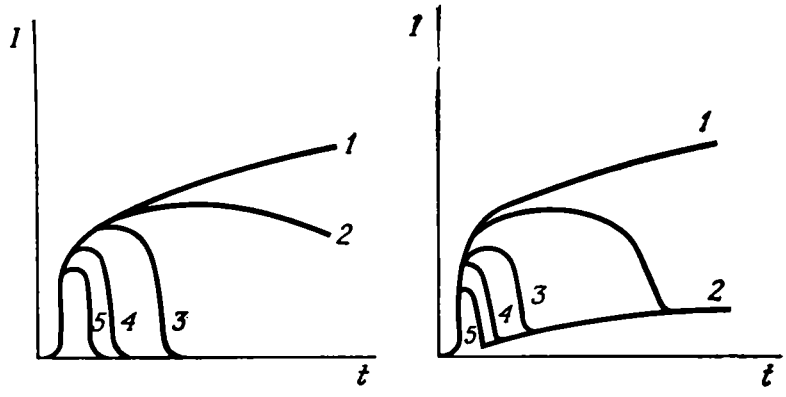

Fig. 18.11. Effect of surface-active substances on the variation of the current during the growth of a single drop:

1—in the absence of surface-active substance; *2-5*—in the presence of different (increasing) amounts of surface-active substances

expanding drop. The shape of a current-time curve undergoes a noticeable change during the growth of a drop if the solution contains a surface-active substance. Besides, the amount of deviation from the normal shape of the curve is legitimately associated with the concentration of such a substance (Fig. 18.11).

18.4. FURTHER DEVELOPMENT OF POLAROGRAPHY

Polarography is developing along the path of increasing the sensitivity and accuracy of the method and extending the range of its potentialities. One of the variants of polarography providing increased sensitivity is the differential polarographic method. In this method, instead of current-potential curves, use is made of derivative curves of $dI/d\varepsilon$ versus ε. Such differential curves can be obtained in two ways. The first procedure consists in using two identical dropping-mercury electrodes in the same solution and applying to one electrode a voltage several millivolts lower than to the other. In the second procedure, one deals, as usual, with a single capillary but makes use of special differentiating electronic circuits. A comparison of a simple polarogram with a differential one is shown in Fig. 18.12. Qualitative and quantitative determinations with the aid of differential polarograms are carried out by measuring potentials and

peak heights. An advantage of such polarograms is the possibility of identifying impurities of less noble metals in a solution containing an excess of ions of more noble metals. This cannot be achieved by means of true polarography.

New possibilities were opened up in polarography when electronic oscillographs entered the scene. These devices are used to register changes in potential and current with time. In the most widespread technique of oscillographic polarography, alternating voltage is impressed upon the cell and a potential-time curve is traced, which

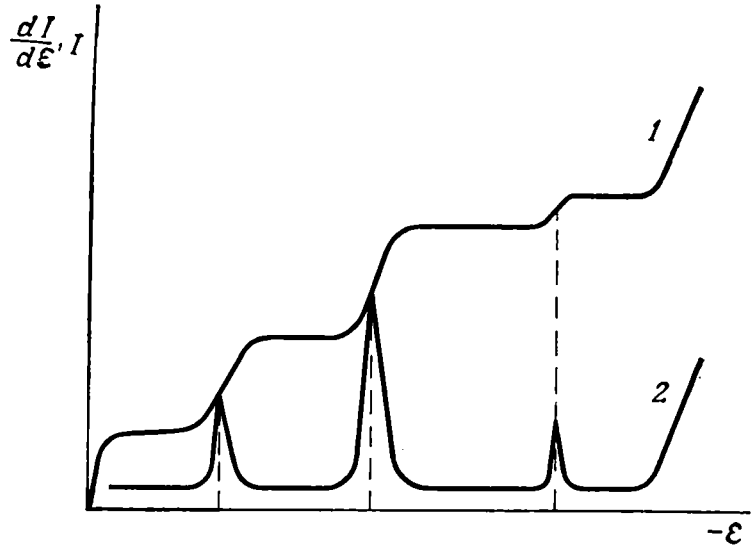

Fig. 18.12. Comparing the curves of ordinary (1) and differential (2) polarography

consists of two portions—the ascending, cathodic branch and the descending, anodic branch. At frequencies of the order of 50 Hz the curve for the supporting electrolyte has the shape of a sine-wave (Fig. 18.13*a*). When the solution contains substances electrochemically active on the dropping-mercury electrode the ascending and descending branches of the potential-time curve show time-lags corresponding respectively to reduction and oxidation of these substances. If these processes are reversible, time-lags appear at approximately the same potential (Fig. 18.13*b*); when they are irreversible the reduction and oxidation potentials are found to be different (Fig. 18.13*c*). When the frequency increases, say to 10^5 Hz, the sawteeth on the potential-time curve extend into lines, forming an oscillopolarographic spectrum. Each line in this spectrum corresponds to the reduction of a definite substance (the anodic branch of the sinusoid is usually omitted from the spectrum). An oscillopolarographic spectrum thus permits determination of the qualitative composition of a solution. For quantitative analysis it is necessary to use derivative oscillopolarographic curves, prefe-

rably $d\varepsilon/dt$ versus ε curves, the shape of which is shown in Fig. 18.14. Each minimum on the oscillopolarogram corresponds to the half-wave potential of a definite ionic species, and its height is propor-

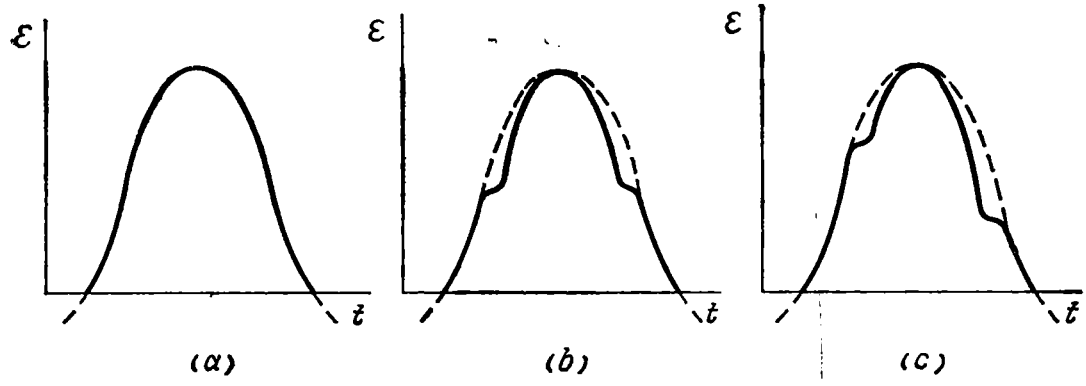

Fig. 18.13. Potential-time curves in oscillographic polarography: *a*—curve for the background electrolyte; *b*—curve obtained in the presence of a substance, the reduction and oxidation of which proceeds reversibly; c—ditto for irreversible processes

tional to the ionic composition. The sawteeth on the cathodic portion of the oscillopolarogram symbolyze lead and cadmium; indium gives no sawtooth under the same conditions. The anodic portion of the

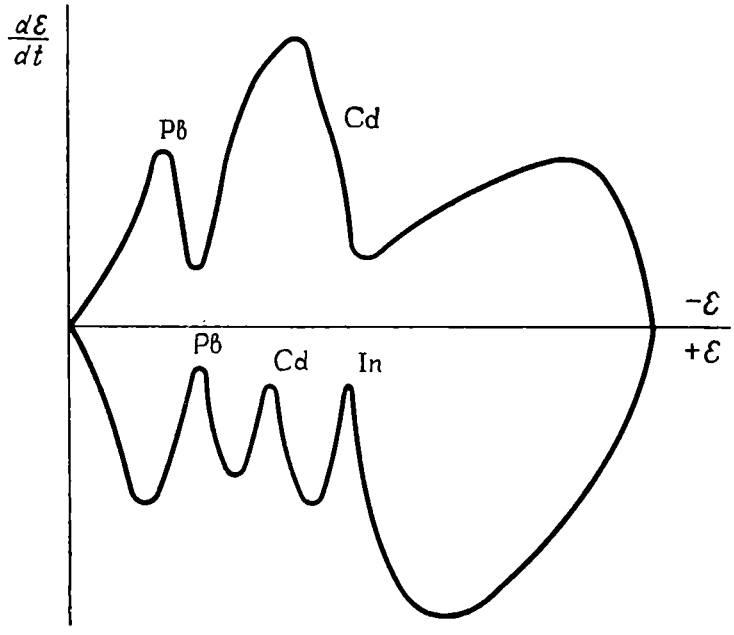

Fig. 18.14. Derivative curves of oscillographic polarography

curve shows three sawteeth, the last one corresponding to indium, oxidizable at a higher potential than cadmium. Combining cathodic and anodic oscillopolarograms widens the possibilities of this method as compared with classical polarography.

PART SIX

The Kinetics of Some Electrode Processes

CHAPTER 19

The Hydrogen Evolution Reaction

19.1. GENERAL DESCRIPTION OF THE PROCESS

The electrolytic evolution of hydrogen in acid and alkaline solutions occurs in different ways. The source of hydrogen in acid solutions is hydroxonium ions which are discharged at the cathode to form hydrogen gas:

$$2H_3O^+ + 2e = H_2 + 2H_2O \qquad (19.1)$$

In the case of alkaline solutions it is assumed that electrons are directly added on to water molecules which then decompose to yield hydrogen and hydroxyl ions:

$$2H_2O + 2e = H_2 + 2OH^- \qquad (19.2)$$

It is believed that reaction (19.2) may also proceed in acid solutions but at high current densities. In certain cases hydrogen is evolved in acidic mediums directly from the molecules of the acid:

$$2HA + 2e = H_2 + 2A^- \qquad (19.3)$$

This case is realizable when hydrogen is evolved at a mercury cathode from aqueous solutions of carbonic acid.

Weak organic bases B are capable of catalyzing the cathodic evolution of hydrogen to form, together with hydrogen ions, positively charged adsorbed particles:

$$B + H_3O^+ = BH^+_{ads} + H_2O \qquad (19.4)$$

These particles are discharged

$$BH^+_{ads} + e = BH_{ads}$$

and the unstable complexes formed are then decomposed into hydrogen and the initial base:

$$BH_{ads} = B + \frac{1}{2}H_2 \qquad (19.6)$$

The acceleration of the hydrogen-evolution reaction is probably associated with the fact that the activation energy in the case of a multistep reaction involving consecutive steps (19.4) to (19.6) is lower than in the direct discharge of hydrogen ions according to (19.1). In neutral mediums, e.g. in salt solutions, the evolution of hydrogen may proceed according to both schemes (19.1) and (19.2). Which mechanism will predominate depends on the solution pH and the nature of the salt. Experimental data obtained in recent years confirm the mechanism of "secondary hydrogen evolution", which was in vogue in the early days of electrochemical science and was later rejected. According to this mechanism the primary act is the discharge of ions of an alkali metal, M^+, with the formation of a corresponding metal or its alloy with the cathode material:

$$M^+ + e = [M] \tag{19.7}$$

Hydrogen is evolved at the subsequent step of interaction of the alkali metal (its alloy or amalgam) with the solvent particles:

$$[M] + H_2O = \frac{1}{2} H_2 + MOH \tag{19.8}$$

This mechanism of hydrogen evolution is most probable in the electrolysis of alkaline solutions or solutions with a high concentration of an alkali-metal salt and on cathodes of high hydrogen overpotential (e.g. mercury, lead). Experimental facts established in investigations of the electroreduction of organic substances (Antropov, Smirnov) point to the incorporation of alkali metals into cathodes made of lead and cadmium. These observations are supported by experimental data obtained by other authors (e.g. Kabanov). For metals of low hydrogen overpotential the secondary evolution of hydrogen is considered less probable. Still, some researchers (e.g. Matsuda) believe that for the formation of hydrogen on platinum cathodes the bulk of experimental data is also best explained by scheme (19.7)-(19.8). Reactions (19.1), (19.2) and (19.3) written in the reverse order will represent the sequence of the anodic dissolution of hydrogen gas with the formation of water, hydroxyl ions or acid molecules.

The hydrogen-evolution reaction at the cathode takes place at a potential ε more negative than the reversible potential ε_H corresponding to the pH of a given solution:

$$\varepsilon_H = \frac{RT}{F} \ln a_{H^+} = -b^0 \mathrm{pH} \tag{19.9}$$

In most cases the difference between the electrode potential arising from the passage of a current on hydrogen evolution and the potential of the equilibrium hydrogen electrode under the same conditions

$$\varepsilon - \varepsilon_H$$

is identified with activation polarization since concentration polarization is small here and may be disregarded. The insignificant role of diffusion limitations in the kinetics of the cathodic hydrogen evolution in acidic solutions will become clear if one takes into account that the mobility of hydrogen ions is considerably high as compared with all other ions. When hydrogen is evolved from alkaline solutions, concentration polarization must be lower owing to the very high concentration of discharging particles (water molecules). Hence, the quantity

$$\varepsilon - \varepsilon_H = \eta_H \tag{19.10}$$

which is known as the hydrogen overpotential (or overvoltage), may be regarded as a direct measure of the irreversibility of the electrochemical hydrogen-evolution process. The value of hydrogen overpotential and its dependence on various factors must therefore be closely related to the nature of the cathodic hydrogen-evolution reaction.

Study of hydrogen overpotential enables one to identify the mechanism of hydrogen evolution and is therefore of great interest from the theoretical point of view. Regularities established for hydrogen overpotential can partly be extended to other cases of electrochemical kinetics, which considerably raises the theoretical significance of works on hydrogen overpotential. Investigation of hydrogen overpotential is also of great practical importance since present-day industrial electrochemistry is primarily the electrochemistry of aqueous solutions and the processes of electrolytic decomposition of water can be superimposed on any cathodic or anodic reaction. The magnitude of hydrogen overpotential constitutes a considerable fraction of the voltage in cells for electrolysis of water and chloride solutions. Knowledge of its nature makes it possible to lower hydrogen overpotential and hence to reduce the consumption of electric power, thereby improving the economic efficiency of these processes. In other cases (electrodeposition of metals, cathodic reduction of inorganic and organic substances, operation of chemical sources of current) knowledge of the nature of hydrogen overpotential allows one to tackle the reverse problem—the search for rational ways of increasing it. All this explains why the study of the cathodic hydrogen-evolution reaction and of the nature of hydrogen overpotential has always attracted the attention of electrochemists.

19.2. DEPENDENCE OF HYDROGEN OVERPOTENTIAL ON CURRENT DENSITY AND ELECTRODE MATERIAL

The dependence of overpotential on current density observed in the evolution of hydrogen from solutions of mineral acids and bases and also from aqueous solutions of salts incapable of dissocia-

ting into surface-active ions may be described by Fig. 16.2 (see page 381) or by Fig. 19.1. In the region of small deviations from the equilibrium potential the relation between overpotential and current density is linear:

$$\eta = Ri \tag{19.11}$$

As the potential moves farther away from the equilibrium value (with increasing current density) the linear relation changes into a semilogarithmic one:

$$\eta = a + b \log i \tag{19.12}$$

For some metals, e.g. mercury, this semilogarithmic relation with constant values of a and b holds up to the highest current den-

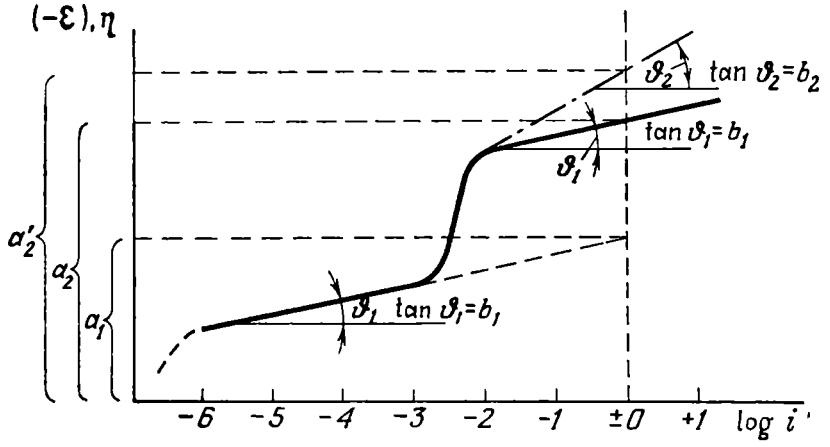

Fig. 19.1. Electrode polarization (electrode potential) versus current density for hydrogen evolution on some metals (after Kolotyrkin)

sities so far attained (see Fig. 16.2). For other metals, e.g. lead and platinum, in a certain region of current densities a new semilogarithmic straight line appears, with a changed and b being the same (lead) or different (platinum) (see Fig. 19.1).

It can be seen from Table 19.1 that the value of a varies widely from metal to metal: from 0.1V for platinum to 1.5V for lead. Apart from the electrode material, the value of a is also affected by the state of the electrode surface. The constant a falls when the electrode surface becomes loosened and free of oxide films. The value of b varies within narrower limits—from 0.03 to 0.12 and only in rare cases (for technical and oxidized metals) does it exceed 0.12. Low values of b are observed for metals of the lowest overpotential (with a minimum value of a), e.g. platinum and palladium. For many metals, including all metals of high overpotential, the value of b is about 0.12.

TABLE 19.1

Values of Constants a and b in Tafel's Equation for Cathodic Hydrogen Evolution on Different Metals, $t = 20 \pm 2°C$

Metal	Acidic solutions		Alkaline solutions		Metal	Acidic solutions		Alkaline solutions	
	a	b	a	b		a	b	a	b
Ag	0.95	0.10	0.73	0.12	Mo	0.66	0.08	0.67	0.14
Al	1.00	0.10	0.64	0.14	Nb	0.8	0.10	—	—
Au	0.40	0.12	—	—	Ni	0.63	0.11	0.65	0.10
Be	1.08	0.12	—	—	Pb	1.56	0.11	1.36	0.25
Bi	0.84	0.12	—	—	Pd	0.24	0.03	0.53	0.13
Cd	1.40	0.12	1.05	0.16	Pt	0.10	0.03	0.31	0.10
Co	0.62	0.14	0.60	0.14	Sb	1.00	0.11	—	—
Cu	0.87	0.12	0.96	0.12	Sn	1.20	0.13	1.28	0.23
Fe	0.70	0.12	0.76	0.11	Ti	0.82	0.14	0.83	0.14
Ge	0.97	0.12	—	—	Tl	1.55	0.14	—	—
Hg	1.41	0.114	1.54	0.11	W	0.43	0.10	—	—
Mn	0.8	0.10	0.90	0.12	Zn	1.24	0.12	1.20	0.12

Measurements carried out in recent years with single crystals of various metals (copper, bismuth, chromium, cadmium, nickel, tin and lead) have shown that the hydrogen overpotential largely depends on the symbol of the single-crystal face on which hydrogen is cathodically evolved. Therefore hydrogen overpotentials found for solid cathodes of polycrystalline structure represent average values. They may vary depending on the percentage of exposure of different crystal faces.

Many attempts have been made to establish a relationship between the hydrogen overpotential on a given metal and some other of its physical properties: catalytic activity with respect to recombination of free hydrogen atoms, melting or evaporation heat, electronic work function, minimum interatomic distance in crystal lattice, compressibility, etc. For example, an inference has been drawn in these studies that the higher is the melting point of a metal the lower will be its hydrogen overpotential; this observation however cannot be accepted even as an approximate rule. Bonhoeffer (1924) found that the higher the catalytic activity of a metal for recombination of hydrogen atoms, the lower is the hydrogen overpotential on it, i.e., in a series of metals these properties increase in opposite directions:

catalytic activity →

Pb, Sn, Zn, Cu, Ag, Fe, Ni, W, Pd, Pt

← hydrogen overpotential

Kobozev (1947) and also Bockris (1951) found a relationship between electronic work function and hydrogen overpotential. Comparing the hydrogen overpotential with the minimum interatomic distance in metals, Khomutov (1950) established that the lowest overpotential is observed on metals with an interatomic distance of about 2.7 Å; the overpotential rises regularly as this distance increases or decreases. In his later works Khomutov noted that the interatomic distance at which the overpotential is minimal is close to the diameter of the water molecule and proposed a modelistic method for calculating the coefficient b in Tafel's equation. According to Lorenz (1950) the following relation exists between the constant a and the electronic compressibility $\varkappa_e$

$$a = 2 - \frac{1}{\sqrt{\varkappa_e 10^6}} \tag{19.13}$$

19.3. EFFECT OF SOLUTION NATURE AND COMPOSITION ON HYDROGEN OVERPOTENTIAL

The greatest number of investigations of hydrogen overpotential have been carried out with aqueous solutions. However, for mercury (and, with lower accuracy, for some other metals) there have also been obtained data in nonaqueous acid solutions. The hydrogen overpotential on mercury during hydrogen evolution from a solution of hydrogen chloride in ethyl and methyl alcohols is lower than for aqueous solutions. Data obtained for mixed solvents are rather uncertain. The nature of the solvent is less important for metals of low overpotential. The relation between the hydrogen overpotential and the solvent nature has not yet been accurately established, though some published data indicate that for copper and nickel the values of hydrogen overpotential are slightly higher in alcohol solutions than in aqueous ones.

The effect of the solution pH on hydrogen overpotential has been studied most thoroughly for mercury cathodes. It has been found that in solutions of pure acids at concentrations up to 0.1 g-eq/litre the hydrogen overpotential is not a function of pH. At higher concentrations the overpotential becomes dependent on pH, decreasing with increasing acid content, the ratio $\Delta\eta/\Delta\text{pH}$ being about 60 mV. If solutions contain an excess of extraneous (indifferent) electrolyte, apart from the acid, the variation of overpotential with pH is also observed at acid concentrations lower than 0.1 g-eq/litre. In alkaline solutions, at an alkali concentration of 0.1 g-eq/litre and higher, the hydrogen overpotential decreases with increasing concentration. In the presence of an excess of extraneous ions this variation of overpotential with pH is also observed for dilute alkaline solutions. The dependence of hydrogen overpotential on pH at mercury in solutions containing a constant excess of extraneous ions is shown

in Fig. 19.2. The maximum hydrogen overpotential is observed in neutral solutions and it falls linearly as the pH value deviates to either side of the neutral point. For concentrated acidic and alkaline solutions the relationship between the hydrogen overpotential and the solution composition becomes more complicated. For nickel the dependence of the overpotential on pH has been observed in solutions of pure acids at concentrations below 0.1 g-eq/litre. In

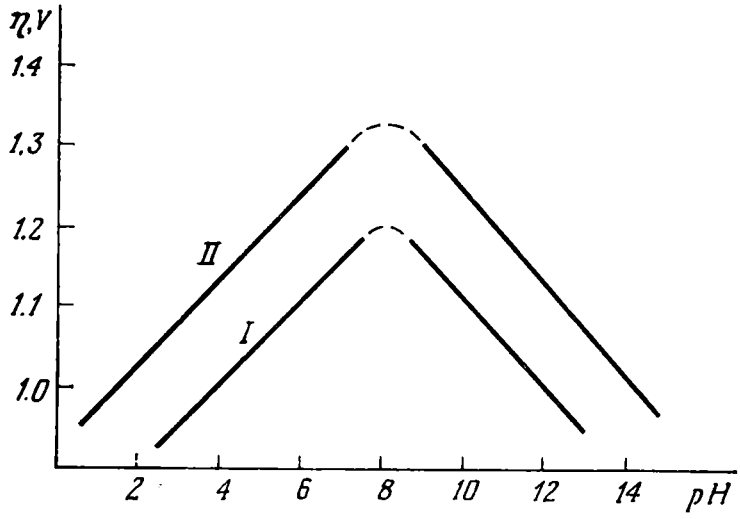

Fig. 19.2. Relation between the overpotential in hydrogen evolution on a mercury cathode and the solution pH at different current densities:
I—1 × 10^{-6} A/cm^2; *II*—1 × 10^{-4} A/cm^2

contrast to mercury, however, in this case the overpotential varies only slightly with pH and does not obey a simple linear law. The hydrogen overpotential on lead and on platinum is almost independent of the solution pH.

Hydrogen overpotential is highly sensitive to the presence of foreign substances in the electrolyte. The addition of salts to dilute acid solutions increases the hydrogen overpotential on mercury; for example, a tenfold increase of the concentration of a uni-univalent electrolyte (at constant pH) increases η approximately by 55-58 mV. The initial addition of an electrolyte with a polyvalent cation exerts a stronger effect than an equal addition of a uni-univalent salt. Substances with surface-active anions have the strongest influence on the hydrogen overpotential on mercury in the region of small current densities, reducing it by tenths of a volt. Conversely, surface-active cations increase the hydrogen overpotential on mercury in a wide range of current density. Surface-active molecular substances either increase or decrease the value of η on mercury depending on their nature. The effect of these substances becomes weaker with increasing current density and comple-

tely disappears at high current densities. For platinum, iron and nickel the hydrogen overpotential also changes (increases) on addition of surface-active substances. The effect of surface-active substances on hydrogen overpotential for these metals, too, is a function of the electrode potential. In the case of iron on which the hydrogen overpotential in acid solutions is only slightly dependent on pH, the presence of surface-active cations in solution not only increases the overpotential but also changes the relation between η and pH.

The introduction into a solution of substances capable of undergoing reduction most often lowers the hydrogen overpotential (at a constant current density), though in some cases the situation is reversed.

19.4. THE EFFECT OF TEMPERATURE AND SOME OTHER FACTORS

The hydrogen overpotential falls with rising temperature, the temperature coefficient being dependent on the metal nature and current density. The character of the temperature variation of

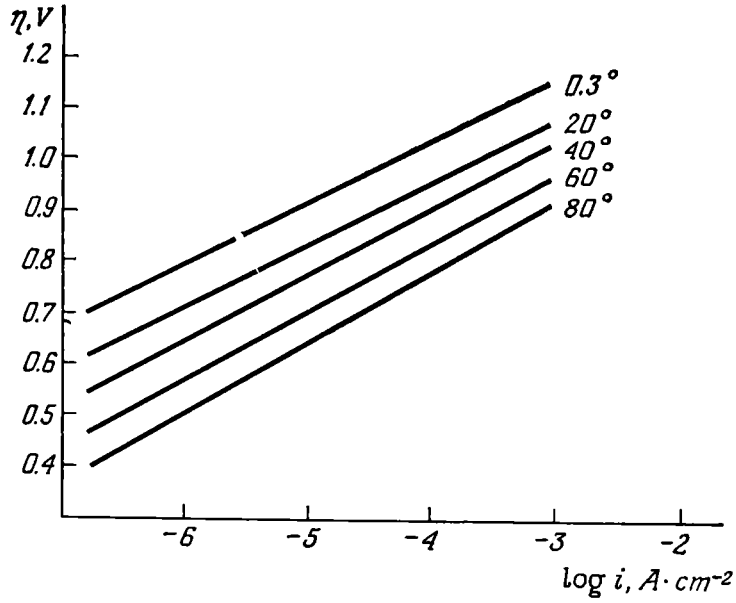

Fig. 19.3. Relation between hydrogen overpotential and logarithm of current density i for mercury at various temperatures

overpotential at a given current density is affected by corresponding changes in the constants a and b in Tafel's equation (Figs. 19.3 and 19.4). Since the constant b increases and the constant a decreases with rise of temperature, it follows that the temperature effect must be stronger in the region of low current densities. On average, the temperature coefficient of overpotential, i.e., the quantity

$(d\eta/dt)_i$, is 1 to 4 mV/°C; the lower limit refers to metals of low overpotential and the upper to those of high overpotential. If it is assumed that the semilogarithmic dependence remains unaltered up to high current densities, the semilogarithmic straight lines may be expected to intersect at a certain current density with the resulting change in the sign of the temperature coefficient of overpotential.

At a given overpotential the temperature dependence of the rate of hydrogen evolution is described by Eq. (17.5). The activation energy of the hydrogen-evolution reaction calculated from

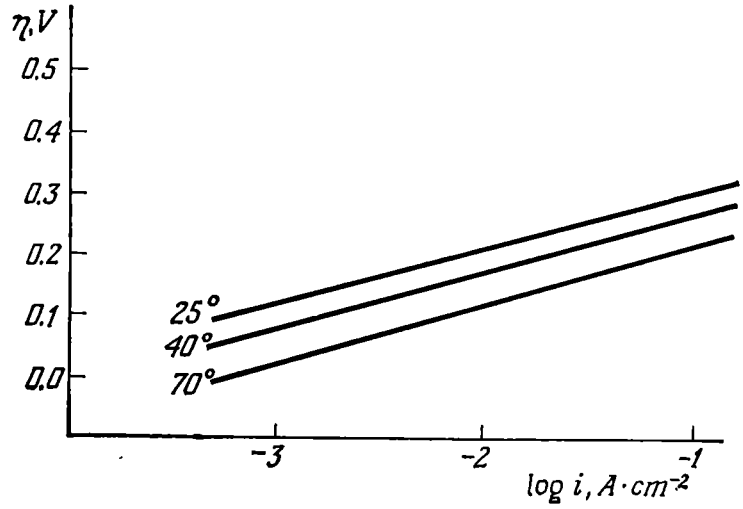

Fig. 19.4. Relation between hydrogen overpotential and logarithm of current density i for tungsten at various temperatures

this equation depends on the hydrogen overpotential. With increasing overpotential it decreases, as a first approximation, according to the linear law. Activation energies extrapolated to zero overpotential depend on the nature of the electrode metal and the solution composition. For example, when hydrogen is evolved from acid solutions containing no surface-active substances, the activation energy of hydrogen evolution is about 22 kcal/mole on mercury and of the order of 16 kcal/mole on tungsten.

The relation between the overpotential and the hydrogen pressure has not been studied sufficiently. According to recent measurements, the overpotential on mercury and a smooth platinum electrode diminishes somewhat with increasing H_2 pressure.

The hydrogen overpotential in the evolution of hydrogen on metals of the iron and platinum groups is affected by ultrasonic vibrations. The hydrogen overpotential undergoes a change under the influence of light radiation and radioactive particles.

19.5. POSSIBLE STEPS AND PATHS FOR THE CATHODIC HYDROGEN EVOLUTION REACTION

Reactions (19.1), (19.2) and (19.3) represent the overall cathodic hydrogen-evolution process under different electrolysis conditions. This process involves a series of consecutive steps and may take different paths depending on the conditions chosen. The first step—the transport to the electrode surface of particles from which hydrogen is cathodically evolved—proceeds almost unhindered here. The next step is the discharge of hydrogen ions (or water molecules) with the formation of adsorbed hydrogen atoms:

$$H_3O^+ + e = H_{ads} + H_2O \qquad (19.14)$$

or

$$H_2O + e = H_{ads} + OH^- \qquad (19.15)$$

Irrespective of whether the discharge occurs from an acidic or alkaline medium, it will produce adsorbed hydrogen atoms [1]. For steady-state electrolysis conditions to be attained it is necessary that the surface concentration of hydrogen atoms be kept constant, i.e., that they be continuously removed from the cathode surface. Hydrogen atoms can be removed in three ways: by catalytic recombination, electrochemical desorption or emission. In the catalytic mechanism hydrogen atoms are recombined into molecules and simultaneously desorbed:

$$H_{ads} + H_{ads} = H_2 \qquad (19.16)$$

the electrode metal serving as the catalyst. Kobozev assumed that, apart from ordinary molecules, there may appear in electrolysis products vibrationally excited hydrogen molecules H_2^* owing to the specificity of an electrochemical process, in which adsorbed hydrogen

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[1] The author of this book has suggested a mechanism for the electrolytic evolution of hydrogen from alkaline solutions, which does not involve the formation of adsorbed hydrogen. According to this mechanism, two associates consisting of two water molecules $(H_2O)_2$ each, to which two electrons add on successively, are discharged:

$$(H_2O)_2 + e = (H_2O)_2^-;\ (H_2O)_2^- + e = (H_2O)_2^{2-};\ (H_2O)_2^{2-} = H_2 + 2OH^-$$

This reaction is analogous to the recombination of two hydrated electrons $\bar{e}_{aq}$:

$$\bar{e}_{aq} + \bar{e}_{aq} = H_2 + 2OH^-$$

A hydrogen evolution reaction in which hydrated electrons $\bar{e}_{aq}$ are involved and no hydrogen adatoms are formed is also possible in principle in the case of acid solutions, especially on cathodes of high overpotential and small heat of adsorption of hydrogen atoms; it may proceed, for example, according to the following scheme:

$$\bar{e}_{aq} + H_3O^+ = H + H_2O$$
$$H + H_3O^+ = H_2^+ \cdot H_2O$$
$$H_2^+ \cdot H_2O + \bar{e}_{aq} = H_2 + H_2O$$

atoms are forced by the electrical current to land on any points of the cathode (including sites with a small heat of adsorption):

$$H^*_{ads} + H^*_{ads} = H^*_2 \tag{19.17}$$

In electrochemical desorption, the hydrogen atoms are removed from the electrode surface as a result of the discharge of hydrogen atoms (or water molecules) on the already adsorbed atoms according to the equations

$$H_3O^+ + H_{ads} + e = H_2 + H_2O \tag{19.18}$$

or

$$H_2O + H_{ads} + e = H_2 + OH^- \tag{19.19}$$

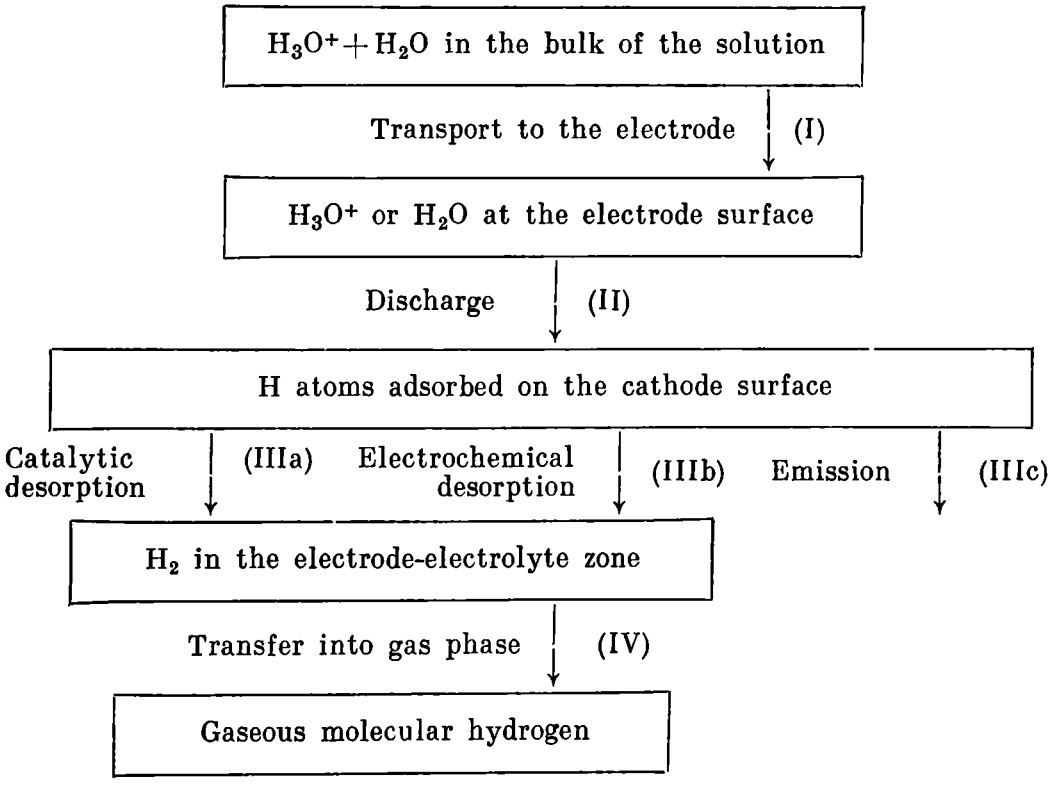
In the emission mechanism, adsorbed hydrogen atoms evaporate from the electrode surface as free atoms:

$$H_{ads} = H \tag{19.20}$$

which then recombine into hydrogen molecules.

The molecular hydrogen formed from the adsorbed atomic hydrogen must be removed from the electrode-electrolyte interface into the gas phase.

Thus, the cathodic hydrogen-evolution process may be represented by the following scheme:



Any one of these four steps may be rate determining and responsible for the appearance of hydrogen overpotential. In the present case the hindrances associated with the transport of substances (step I) are not essential. There is evidence, however, that at high current densities in acid solutions the discharge step should be described by Eq. (19.2) rather than by Eq. (19.9) owing to the slow rate of the transport of H_3O^+ ions.

In the electrochemical hydrogen-evolution reaction the removal of adsorbed hydrogen atoms can be effected in several ways. If this step (step III in the above scheme) is slow, then the rate of the overall process must be determined by the rate of the most effective of the above-indicated three desorption mechanisms. Slow recombination, for example, implies that the catalytic formation of hydrogen molecules is more strongly hindered than the discharge or transport step and at the same time proceeds much faster than electrochemical desorption or emission of hydrogen atoms. At close values of the rate constants of parallel steps the removal of hydrogen may occur in several ways simultaneously [1].

Let the slow step be denoted by A and the most effective step, the removal of adsorbed atomic hydrogen, by B; then the most probable combinations of these two steps can be represented as shown in Table 19.2.

TABLE 19.2

Possible Combinations of the Slow (A) and Fast (B) Steps of the Cathodic Evolution of Hydrogen

Mechanism	Discharge	Recombination	Electrochemical desorption	Removal of dissolved hydrogen
Volmer-Tafel	A	B	—	—
Volmer-Heyrovsky	A	—	B	—
Tafel-Horuiti	—	AB	—	—
Heyrovsky-Horuiti	—	—	AB	—
Diffusion	—	—	—	AB

The Volmer-Tafel mechanism corresponds to the case where the discharge step runs slow and the removal of hydrogen atoms is accomplished by recombination. According to the Volmer-Heyrovsky mechanism, the discharge is the slow step (rds) again, but the hydrogen atoms are removed by electrochemical desorption. In the Tafel-Horuiti mechanism the recombination of hydrogen atoms determines

[1] The problem of hydrogen removal from the cathode surface, which is of great importance for the understanding of the nature of the hydrogen evolution reaction was the subject of dispute between Kobozev's and Frumkin's schools (1940-56).

the rate of the overall reaction and at the same time removes the hydrogen atoms formed in the discharge step, which proceeds without hindrances. The Heyrovsky-Horuiti mechanism is based on the assumption that the overall rate is determined by the electrochemical-desorption step, which is also the most effective way for removing the adsorbed hydrogen. In the diffusion mechanism all the steps run faster than the removal of the molecular hydrogen dissolved in the electrolyte layer adjacent to the electrode surface. Apart from the mechanisms listed in Table 19.2, other kinetic variants of the occurrence of the cathodic hydrogen-evolution reaction are also possible. For example, it may happen that the rate constants of two or more steps differ little from one another. When the conditions under which the reaction takes place change, one mechanism may be replaced by another. When the conditions on one and the same electrode remain constant, there may appear sites on it where hydrogen evolution will take place in different ways because of the inhomogeneity of the electrode surface.

The possibility of one kinetic mechanism being replaced by another was considered by Hammett (1933) and in a more general way by Loshkarev and Esin (1938), and also by other authors.

The actual mechanism of the cathodic hydrogen-evolution reaction on a given metal can be established on the basis of comprehensive experimental investigations and comparison of the results obtained with the inferences following from the theories of different types of overpotential.

19.5.1. ELECTROCHEMICAL OVERPOTENTIAL IN THE HYDROGEN EVOLUTION REACTION

Electrochemical Reaction on the Free Metal Surface. If out of the two possible variants of the discharge of hydroxonium ions or water molecules—on a free cathode surface and on the already adsorbed hydrogen atoms—the first is realized, then it may be described by kinetic equations (16.80) and (16.81). Assuming that $c_{H_2O} = \text{const}$ and $\theta_H \neq f(i)$ and is very small ($\theta_H \ll 1$), these equations may be rewritten thus:

$$i = \vec{i} - \overleftarrow{i} = Fe^{(\alpha-1)\mp\zeta/RT}(\vec{k}c_{H_3O^+}e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}\theta_H e^{(1-\alpha)\,F\varepsilon/RT}) \quad (19.21)$$

for acidic solutions and

$$i = \vec{i} - \overleftarrow{i} = Fe^{\alpha F\zeta/RT}(\vec{k}c_{H_2O}e^{-\alpha F\varepsilon/RT} - \overleftarrow{k}c_{OH^-}\theta_H e^{(1-\alpha)\,F\varepsilon/RT}) \quad (19.22)$$

for alkaline solutions. When $\varepsilon = \varepsilon_r$ and $i = 0$, then $\vec{i} = \overleftarrow{i} = i^0$ and therefore one can write in place of Eqs. (19.21) and (19.22):

$$i = \vec{i} - \overleftarrow{i} = i^0_{acid}e^{(\alpha-1)F\zeta/RT}(e^{-\alpha F\eta/RT} - e^{(1-\alpha)F\eta/RT}) \quad (19.23)$$

and

$$i = \vec{i} - \overleftarrow{i} = i^0_{alk} e^{\alpha F\zeta/RT} (e^{-\alpha F\eta/RT} - e^{(1-\alpha)F\eta/RT}) \qquad (19.24)$$

respectively.

The quantity i^0_{acid} is given by the expression

$$i^0_{acid} = F\vec{k}c_{H_3O^+} e^{-\alpha F\varepsilon_r/RT} = F\overleftarrow{k}\Theta_H e^{(1-\alpha)F\varepsilon_r/RT}$$

or since

$$_H\varepsilon_r = \varepsilon^0_H + \frac{RT}{F} \ln \frac{c_{H_3O^+}}{c_H}$$

and

$$\Theta_H \approx c_H, \quad \varepsilon^0_H = \text{const}$$

it follows that

$$i^0_{acid} = F\vec{k}' c^{(1-\alpha)}_{H_3O^+} c^{\alpha}_H = F\overleftarrow{k}' c^{(1-\alpha)}_{H_3O^+} c^{\alpha}_H = {}_{st}i^0_{acid} c^{(1-\alpha)}_{H_3O^+} c^{\alpha}_H \qquad (19.25)$$

Under the same conditions the quantity i^0_{alk} is determined by the expression

$$i^0_{alk} = {}_{st}i^0_{alk} c^{\alpha}_{OH^-} c^{\alpha}_H \qquad (19.26)$$

since

$$c_{H_3O^+} \cdot c_{OH^-} = K_w$$

At a considerable cathodic overpotential Eqs. (19.23) and (19.24) simplify to

$$i_{acid} = \vec{i} = {}_{st}i^0_{acid} c^{1-\alpha}_{H_3O^+} c^{\alpha}_H e^{(\alpha-1)F\zeta/RT} e^{-\alpha F\eta/RT} \qquad (19.27)$$

and

$$i_{alk} = \vec{i} = {}_{st}i^0_{alk} c^{\alpha}_{OH^-} c^{\alpha}_H e^{\alpha F\zeta/RT} e^{-\alpha F\eta/RT} \qquad (19.28)$$

Taking logarithms of Eq. (19.27) and solving it for η, one gets the following expression

$$\eta = \frac{RT}{\alpha F} \ln {}_{st}i^0_{acid} c^{\alpha}_H + \frac{RT}{F} \frac{1-\alpha}{\alpha} \ln c_{H_3O^+} - \frac{1-\alpha}{\alpha} \zeta - \frac{RT}{\alpha F} \ln i_{acid} \qquad (19.29)$$

or, after changing to common logarithms and substituting the constant a for the first term,

$$\eta = a + 2.3 \frac{RT}{F} \frac{1-\alpha}{\alpha} \log c_{H_3O^+} - \frac{1-\alpha}{\alpha} \zeta - 2.3 \frac{RT}{\alpha F} \log i_{acid} \qquad (19.30)$$

From Eq. (19.30) it follows that in concentrated acid solutions or in acid solutions of any concentration but containing an excess of extraneous ions the overpotential at a given current will diminish at room temperature by $(1 - \alpha)/\alpha$ 0.06V for a tenfold increase

of the hydrogen-ion concentration (i.e., a unit decrease of pH). Indeed, under the conditions chosen the ζ potential must be very small and constant. A change in the concentration of an acid (hydrogen ions) will affect the overpotential only through the second term of Eq. (19.30). Conversely, in dilute acid solutions a change in the acid concentration will not only determine $c_{H_3O^+}$ but also affect the value of the ζ potential. From the Stern theory it follows that the value of ζ must vary in the given case with the acid concentration equal to the hydrogen-ion concentration according to the equation

$$\zeta = \text{const} + \frac{RT}{F} \ln c_{H_3O^+} \tag{19.31}$$

Substituting this value of ζ into Eq. (19.30) leads to the equation

$$\eta = a + 2.3 \frac{RT}{F} \frac{1-\alpha}{\alpha} \log c_{H_3O^+} - 2.3 \frac{RT}{F} \frac{1-\alpha}{\alpha} \log c_{H_3O^+} - \\ - 2.3 \frac{RT}{\alpha F} \log i_{acid} = a - 2.3 \frac{RT}{\alpha F} \log i_{acid} \tag{19.32}$$

from which it follows that the hydrogen overpotential in dilute acid solutions is independent of the acid concentration.

From Eq. (19.28) it follows that in alkaline solutions the following equation holds for the hydrogen overpotential:

$$\eta = \frac{RT}{\alpha F} \ln {}_{st}i^0_{alk} c^{\alpha}_{H} + \frac{RT}{F} \ln c_{OH^-} + \zeta - \frac{RT}{\alpha F} \ln i_{alk} \tag{19.33}$$

or

$$\eta = a + 2.3 \frac{RT}{F} \log c_{OH^-} + \zeta - 2.3 \frac{RT}{\alpha F} \log i_{alk} \tag{19.34}$$

Thus, in concentrated alkaline solutions or in alkaline solutions of any concentration but containing an excess of indifferent electrolyte, where the ζ potential may be taken as constant and close to zero, the overpotential at a constant current density and room temperature will fall by 0.06V for a 10-fold increase of the concentration of hydroxyl ions (or a unit increase of pH). In dilute alkaline solutions containing no indifferent electrolyte the ζ potential will be a function of the concentration of the alkali (OH^- ions):

$$\zeta = \text{const} + \frac{RT}{F} \ln c_{OH^-} \tag{19.35}$$

Substituting this value of ζ into Eq. (19.34) yields the equation

$$\pi = a + 2.3 \frac{RT}{F} \log c_{OH^-} + 2.3 \frac{RT}{F} \log c_{OH^-} - 2.3 \frac{RT}{\alpha F} \log i_{alk} = \\ = a + 2 \times 2.3 \frac{RT}{F} \log c_{OH^-} - 2.3 \frac{RT}{\alpha F} \log i_{alk} \tag{19.36}$$

from which it follows that in this case the tenfold increase of c_{OH^-} (the unit increase of pH) decreases the hydrogen overpotential by 0.12V.

Since the ζ potential is a function of the nature and concentration of dissolved substances, the electrochemical hydrogen overpotential must depend on the solution composition. The ζ potential and hence η must be most strongly affected by polyvalent ions and surface-active substances. An analysis of Eqs. (19.29) and (19.33) with account taken of the characteristics of the ζ potential leads to the conclusion that the introduction of extraneous cations must increase, and that of extraneous anions decrease the electrochemical overpotential in the cathodic hydrogen-evolution reaction.

From Eqs. (19.29) and (19.33) it also follows that the overpotential must diminish under the influence of all factors that increase the exchange current. The most important factors are the nature of the electrode metal and of the solvent. The effect of these factors on the electrochemical overpotential can be qualitatively estimated in a rather convenient way by the potential-curve method proposed by Horuiti and Polanyi in 1935. Using this method, these authors described the cathodic hydrogen-evolution reaction and deduced a qualitatively correct relationship between the electrochemical overpotential and the current density. We shall consider here, as an example, only the evolution of hydrogen from acid solutions. The electrochemical act corresponds in this case to the transition of the proton from the hydrated-ion state to the state of a hydrogen atom adsorbed on the metal. In the course of this process the energy undergoes a change along the profile shown on the potential diagram in Fig. 19.5. The left solid curve *ABD* shows the variation of the free energy of the hydrated proton as a function of the distance between the proton and the water molecule. In going from left to right in the direction of the electrode surface, i.e., in the direction of the discharge, the potential energy will increase (as a result of the work done to stretch the $H_2O—H^+$ bond, i.e., to partially dehydrate the hydrogen ion). The right solid potential curve corresponds to the increase (or decrease) of the free energy of the H—M system as a function of the distance between the adsorbed hydrogen atom and the metal surface. When going in the same direction (from the point of intersection of the curves) the potential energy falls under the influence of attractive forces arising between the metal surface and the hydrogen atom. The minimum of the right curve corresponds to the equilibrium position of the adsorbed hydrogen atom, i.e., to the M—H bond. Thus, the variation of the potential energy of a hydrogen ion during the discharge process is described by the potential-curve portion *ABC*. The change of the energy along the path *CBA* corresponds to the reverse process—the ionization of an adsorbed hydrogen atom with the formation of a hydrated hydrogen

ion. If an electron were not added at point B during discharge (or lost during ionization), then the left and right curves would extend to levels D and F, respectively. The D level characterizes the potential energy of the system $H^+ + H_2O$ consisting of a free gaseous proton and liquid water. The distance between levels D and A gives the total real hydration energy of a hydrogen ion, $-\Delta G_{H^+}$. The F level corresponds to the potential energy of the system H + M

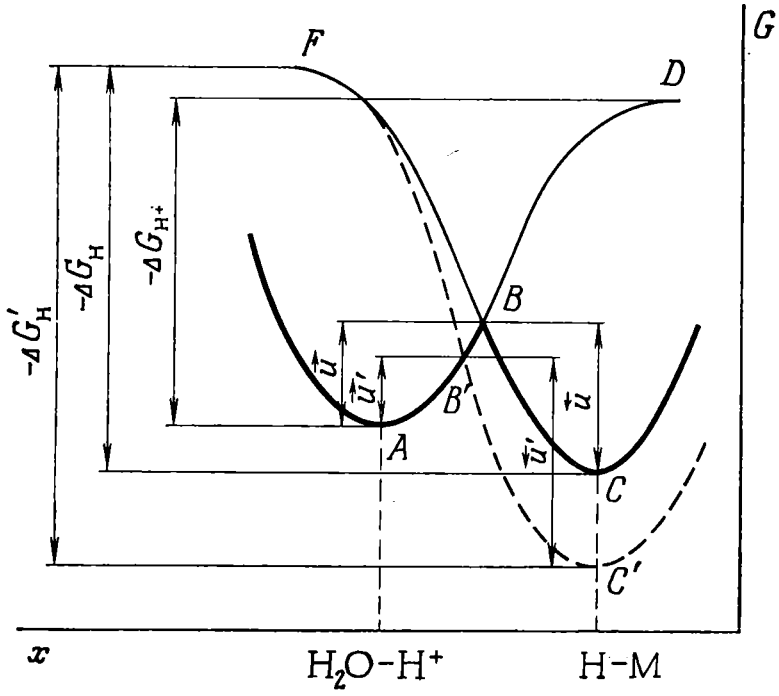


Fig. 19.5. Effect of the heat of adsorption of hydrogen on a metal on the free-energy change in the discharge step $H_3O^+ + e = H_{ads} + H_2O$

consisting of free gaseous hydrogen atoms and a solid metal. The distance between F and C gives the energy of adsorption of atomic hydrogen on the electrode metal, $-\Delta G_H$. From Fig. 19.5 it follows that the activation energy of the discharge step is lower than the total dehydration energy. Similarly, the activation energy of ionization is lower than the energy of desorption of a hydrogen atom from the metal surface. For instance, the activation energy of the discharge of hydrogen ions on mercury at zero overpotential is about 20 kcal/g-ion, while the hydration energy of hydrogen ions is close to 250 kcal/g-ion. Nevertheless, according to the model the activation energy of discharge and hence the hydrogen overpotential must depend on the solvation energy of hydrogen ions and on the energy (or heat) of adsorption of hydrogen atoms[1]. If one confines

[1] In fact, the solvation energy determines the standard potential; its relation to the hydrogen overpotential is indirect and more complicated.

himself to aqueous solutions, for which the position of the left curve remains practically unchanged, then the point of its intersection with the right potential curve will be the lower, the greater is the heat of adsorption. In going from a metal with an adsorption heat $-\Delta G_H$ to a metal with an adsorption heat $-\Delta G'_H$ (the right dashed curve) the activation energy diminishes by an amount $\vec{u} - \vec{u}'$, which is a certain fraction of the increment of the adsorption energy $-(\Delta G'_H - \Delta G_H)$ of hydrogen. For this reason the electrochemical

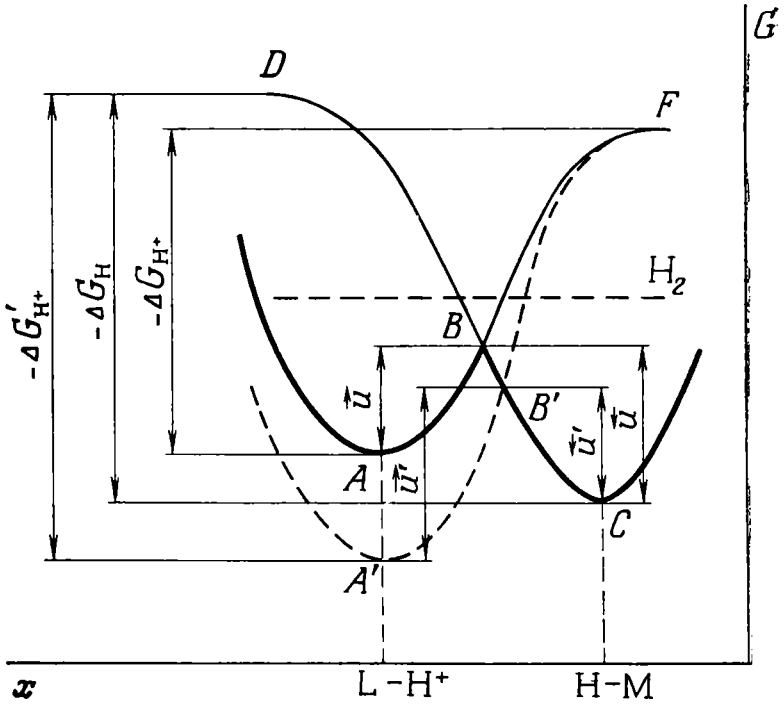


Fig. 19.6. Effect of the heat of solvation of hydrogen ions on the free-energy change in the discharge step $H^+L + e = H^+ + L$

hydrogen overpotential must regularly fall with increasing adsorption capacity of the electrode metal with respect to hydrogen atoms. On the other hand, when hydrogen evolves on a given metal the electrochemical overpotential must depend on the energy state of an ion in solution. Therefore the overpotential should be expected to vary also from solvent to solvent. It can be seen from Fig. 19.6 that the hydrogen overpotential increases in going from a solvent in which the energy of solvation of the proton is lower to a solvent with a higher solvation energy.

Electrochemical Reaction on a Metal Surface Occupied by Adsorbed Hydrogen Atoms. In this case hydrogen evolution proceeds according to schemes (19.2) and (19.3):

$$H_3O^+ + H_{ads} + e = H_2 + H_2O$$

and

$$H_2O + H_{ads} + e = H_2 + OH^-$$

and its kinetics is described by Eqs. (19.4) and (19.5). As follows from the reaction equations, simultaneously with the charge transfer step the adsorbed hydrogen atoms are taken off from the electrode surface and removed in the form of molecules. It is for this reason that this type of electrochemical hydrogen overpotential is often called *electrochemical desorption.*

The concept of the electrochemical desorption as a step determining the rate of the overall cathodic hydrogen-evolution reaction was first formulated by Heyrovsky in 1925. According to Heyrovsky, the electrolytic evolution of hydrogen consists of three steps:

$$1.\ H^+ + e = H$$
$$2.\ H + e = H^-$$
$$3.\ H^+ + H^- = H_2$$

The first two steps proceed without difficulties, while the third step, electrochemical desorption, runs slow. Using Heyrovsky's views and assuming that the concentration of hydrogen ions near the electrode surface is related to their bulk concentration by the Langmuir adsorption isotherm, Gerasimenko and Shlendik (1930) derived the following relation for the cathodic potential

$$\varepsilon = \text{const} - \frac{RT}{F} \ln i + \frac{RT}{F} \ln \frac{Ac_{H^+}^2}{1 + Bc_{H^+}} \qquad (19.37)$$

where A and B are the constants in the Langmuir isotherm. Though the Heyrovsky-Herasymenko-Šlendyk theory contains a number of assumptions which cannot be considered valid at present, it is nevertheless of considerable interest. It can be regarded as the first attempt to take into account the adsorption of hydrogen ions and the effect of the solution composition (pH and extraneous electrolytes) on the hydrogen overpotential. For example, from this theory it follows that in acid solutions containing a constant excess of an extraneous salt the overpotential should be expected to increase by 2.3 RT/F upon 10-fold dilution of the acid. The same conclusion follows from the modern theory of slow discharge.

Later, the Heyrovsky theory was substantially developed by Horuiti and his colleagues (1936). According to Horuiti, the electrochemical desorption of hydrogen in the electrolysis of acid solutions proceeds as follows. The first step is the discharge and the formation of a hydrogen atom adsorbed by a metal H—M:

$$H_3O^+ + e + M = H{-}M + H_2O \qquad (19.38)$$

The adsorbed hydrogen atom interacts with an adsorbed hydroxonium ion to form an intermediate complex:

$$H-M+H^+-H_2O=H_2O\begin{matrix}H\\ \diagup\quad\diagdown\\ H^+\end{matrix}M \qquad (19.39)$$

In this complex the particles H and H^+ are arranged symmetrically relative to the axis of the bond between the water molecule and the metal (H_2O — M), forming a molecular ion H_2^+, which is bound to both the metal surface and the water molecule. The bonding with the metal is provided by a valency electron and that with the water molecule by the net positive charge of the ion. An intermediate complex may also appear when there is no discharge act and no adsorbed hydrogen atom is formed. For this to occur it is necessary that one of the two neighbouring adsorbed hydrogen ions accept an electron. Thus, according to Horuiti, electrochemical desorption does not necessarily proceed via the discharge of an hydroxonium ion on the metal surface already partly covered with hydrogen atoms.

The next step is the discharge of the intermediate complex:

$$H_2O\begin{matrix}H\\ \diagup\quad\diagdown\\ H^+\end{matrix}M-e=H_2+H_2O+M \qquad (19.40)$$

or

$$H^+_{2(ads)}+e=H_2 \qquad (19.41)$$

since the intermediate complex corresponds to an adsorbed molecular hydrogen ion. At this last stage, the addition of an electron is accompanied by the rupture of the bonds in the complex and by the formation of a hydrogen molecule, which is desorbed and removed from the electrode-electrolyte interface. The bond rupture in the intermediate complex and the strengthening of the bonds between the hydrogen atoms is associated with a radical intramolecular rearrangement and requires considerable activation energy. Therefore this step may be regarded as slow and determining the rate of the overall hydrogen-evolution process.

The Horuiti theory takes into account the degree of surface coverage with hydrogen atoms and ion-molecules and also the character of interaction between adsorbed particles. In the simplest case the equations derived by Horuiti transform into Tafel's formula.

19.5.2. THE CHEMICAL (REACTION) OVERPOTENTIAL IN HYDROGEN EVOLUTION

The assumption that the hydrogen overpotential is determined by the rate of the reaction

$$H_{ads}+H_{ads}=H_2$$

i.e., is caused by the slow recombination of hydrogen atoms into molecules (catalytic desorption) was first suggested by Tafel in 1905

and formed the basis of the first quantitative treatment of electrode kinetics.

If the recombination is the slow step, then for the hydrogen evolution reaction to proceed at a specified rate on the metal surface an excess of hydrogen atoms is needed compared with equilibrium conditions. At equilibrium, i.e., at the reversible value of the hydrogen electrode potential, all steps of the electrode reaction are in detailed equilibrium:

$$H_3O^+ \rightleftarrows H_3O^+_{ads} \underset{(H_2)}{\overset{(H)}{\rightleftarrows}} H_{ads}$$

For example, to a definite partial pressure of molecular hydrogen, p_{H_2}, there corresponds the equilibrium surface concentration of hydrogen atoms, $c'_{H(r)}$. The usual equation for the reversible hydrogen electrode

$$\varepsilon = \varepsilon^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{p_{H_2}^{1/2}}$$

may therefore be replaced with the following equation

$$\varepsilon = \varepsilon'^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{c'_{H(r)}} \tag{19.42}$$

which contains $c'_{H(r)}$ in place of p_{H_2}. The rate of the recombination of adsorbed atoms, $\vec{i}$, under equilibrium conditions is equal to that of the reverse reaction—the adsorption of hydrogen molecules from the gas phase with their simultaneous dissociation into atoms, $\overleftarrow{i}$. The currents $\vec{i}$ and $\overleftarrow{i}$ in this case are equal to the exchange current with respect to hydrogen at the recombination-dissociation step, i_r^0.

Assuming that the rate of recombination corresponds to a bimolecular reaction and the rate of the adsorption of hydrogen molecules (with the simultaneous dissociation and formation of adsorbed hydrogen atoms) is proportional to their bulk concentration c_{H_2}, one can write

$$\vec{i} = k_1 c^2_{H(r)} \tag{19.43}$$

and

$$\overleftarrow{i} = k_2 c_{H_2} \tag{19.44}$$

When the reaction proceeds in the cathodic direction, the rate of the process expressed by the quantity i_c equal, by definition, to

$$i_c = \vec{i} - \overleftarrow{i}$$

may be written in the form

$$i_c = \vec{i} - r_r^0 \tag{19.45}$$

if it is assumed that the rate of the reverse reaction does not change since the concentration of molecular hydrogen in the gas phase remains constant. As follows from Eq. (19.43) the final value of i_c, i.e., the excess of $\vec{i}$ over $\overleftarrow{i}$ or i_r^0, can be obtained if the surface concentration of hydrogen atoms during the cathodic process is higher than that corresponding to equilibrium:

$$c'_{H(i)} > c'_{H(r)}$$

where $c'_{H(i)}$ is the surface concentration of atomic hydrogen at a current density i. This new value of the concentration of adsorbed hydrogen atoms does not correspond to the pressure of gaseous molecular hydrogen, which remains constant. Consequently, the slow recombination disturbs the equilibrium between the adsorbed and the gaseous hydrogen. At the same time the theory of slow recombination postulates the retainment of equilibrium between adsorbed hydrogen atoms and hydrogen ions. It is therefore thought that Nernst's formula (19.42) for the reversible hydrogen electrode is also applicable to the cathodic evolution of hydrogen, especially when the deviation from the equilibrium state is not too great. Thus, the hydrogen electrode potential under an external current may be written as

$$\varepsilon_i = \varepsilon'^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{c'_{H(i)}} \tag{19.46}$$

and the hydrogen overpotential due to the slow recombination can be described by the equation

$$\eta = \varepsilon_i - \varepsilon_r = \frac{RT}{F} \ln \frac{c'_{H(r)}}{c'_{H(i)}} = -\frac{RT}{F} \ln \frac{c'_{H(i)}}{c'_{H(r)}} \tag{19.47}$$

Equation (19.47) was derived earlier as a special case of the chemical overpotential caused by the slow occurrence of the purely chemical step following the discharge act (see p. 336).

Equation (19.43) for the rate of recombination, with account taken of Eq. (19.44), yields the following expression for the hydrogen overpotential within the framework of the slow-recombination theory:

$$\eta = -\frac{RT}{F} \ln \left(\frac{i_c + i_r^0}{i_r^0} \right)^{1/2} = -\frac{RT}{2F} \ln \left(1 - \frac{i_c}{i_c^0} \right) \tag{19.48}$$

If

$$\frac{i_c}{i^0} \gg 1$$

Eq. (19.48) reduces to Tafel's formula:

$$\eta = a + b \log i$$

where

$$a = 2.3 \frac{RT}{2F} \log i_r^0, \quad b = -2.3 \frac{RT}{zF}$$

At small deviations from the equilibrium state when i_c only slightly exceeds the exchange current i_r^0, the expression

$$\ln \left(1 + \frac{i_c}{i_r^0}\right)$$

may be taken, after it is expanded into a series, as approximately equal to i_c/i_r^0. In this case one can write in place of Eq. (19.48):

$$\eta = -\frac{RT}{2F} \frac{i_c}{i_r^0} = -R_r i_c \tag{19.49}$$

where R_r is the polarization resistance at the recombination step.

The theory of slow recombination as presented above should be regarded as a first approximation to reality. This approximation corresponds to the idealized case where the cathode surface is homogeneous with respect to energy and no interaction forces operate between adsorbed hydrogen atoms. In actual conditions of hydrogen evolution these assumptions may not be justified, in which case the relation between potential and current density must assume a different form.

The theory of slow recombination was generalized in the works of Horuiti *et al.* (1936-38), Kobozev *et al.* (1937-46), Temkin (1941) and other authors. According to these authors, taking into account the surface inhomogeneity and the interaction forces between adsorbed atoms leads to the appearance of a multiplier $1/\beta$ in the logarithmic coefficient of Eq. (19.48). The factor β may be regarded as a quantity characterizing the adsorption of hydrogen atoms and reflecting the type of the adsorption isotherm. In the simplest case it corresponds to the exponent in Freundlich's adsorption equation:

$$c' = k_F c^{\beta} \tag{19.50}$$

where c' and c = surface and bulk concentrations of a given species of particles, respectively

k_F = Freundlich constant equal to the surface concentration at a bulk concentration of $c' = 1$

β = exponent which depends on the nature of the metal and of adsorbed particles and lies between zero and unity.

Therefore, for metals capable of perceptibly adsorbing hydrogen the expressions for Tafel constants within the framework of the slow-

recombination theory should be written as:

$$a = 2.3\frac{RT}{2\beta F}\log i_r^0 \tag{19.51}$$

$$b = -2.3\frac{RT}{2\beta F} \tag{19.52}$$

In contrast to the slow-recombination theory in its original version, where the coefficient b at a specified temperature is a certain constant equal for all metals, in this case it becomes a function of the nature of the metal and may assume different values, depending on the value of β. This circumstance however does not affect the form of Eq. (19.49), which remains the same as in the original theory.

According to the slow-recombination theory the overpotential is independent of the solution pH [see Eq. (19.48)], though a certain, very slight effect of pH associated with the dipolar nature of the M—H bond can be detected.

19.6. THE NATURE OF HYDROGEN OVERPOTENTIAL ON DIFFERENT METALS

Certain assumptions as to the most probable mechanism of hydrogen evolution on different metals can be made on the basis of general conceptions of electrochemical kinetics concerning this particular electrode reaction. For example, it has been assumed that with increasing heat of adsorption of hydrogen atoms on the cathode metal the probability of a slow discharge diminishes and that of a slow recombination increases. This is associated with the different effect of the variation of the adsorption heat of hydrogen atoms on the rate of discharge and of recombination. As follows from the potential curves (see Fig. 19.5), the activation energy of the discharge step diminishes with increasing adsorption heat. Conversely, the activation energy of the recombination process increases as the bonding (the quantitative characteristic of which is the heat of adsorption) between the metal and the surface hydrogen atoms becomes stronger. At the same time the increase of the adsorption heat must increase the surface concentration of hydrogen atoms and hence the rate of recombination, i.e., produce the reverse effect. The superposition of the two opposite effects may retard or accelerate the recombination step with increasing adsorption heat, but the accelerating effect must always be weaker than in the case of the discharge step. Though data on the heat of adsorption of hydrogen on metals are scarce and contradictory, it can nevertheless be asserted that the heat of adsorption of hydrogen on mercury, zinc and cadmium is much lower than on metals of the platinum and iron groups. Thus, the conditions on mercury, for example, are more favourable for a slow discharge and

those on nickel for a slow recombination. These considerations expressed by Antropov in 1949 led him to the conclusion that there are two extreme groups of metals with different hydrogen overpotential mechanisms. One group includes metals of the platinum and iron groups possessing high adsorption capacity with respect to hydrogen. The recombination step on these metals must play the decisive role in the kinetics of the cathodic hydrogen evolution reaction. The other group covers mercury, lead, cadmium and other metals which are almost incapable of adsorbing hydrogen. For these metals the rate of hydrogen evolution is controlled by the discharge step. Similar views were expounded later by other researchers, e.g., Conway and Bockris.

Plausible assumptions can also be made as to which path predominates in the removal of adsorbed hydrogen atoms by using data on the coverage of the surface with adsorbed hydrogen atoms.

The rate of discharge depends on the hydrogen-atom concentration to the first power, and the rate of recombination, on the concentration to the second power. Therefore, for metals which adsorb hydrogen weakly the removal of hydrogen from their surface must be predominantly accomplished by electrochemical desorption. Conversely, for metals of high adsorption capacity with respect to hydrogen atoms the most effective way is the removal of these atoms by catalytic recombination (Frumkin).

These general inferences as to the nature of overpotential on various metals are confirmed by the agreement between the most important corollaries of the hydrogen-overpotential theory and experimental data on the kinetics of hydrogen evolution. For instance, none of the methods has succeeded in detecting any traces of adsorbed atomic hydrogen on the mercury surface in the region of potentials for the cathodic evolution of H_2. Hence the removal of hydrogen is not rate limiting. The value of the logarithmic coefficient b for mercury is close to 0.12. Considering that the coverage of the mercury cathode surface with adsorbed atomic hydrogen is negligibly small this value of b cannot be obtained from the slow-recombination theory. Experimental data on the effect of the solution composition and pH on overpotential in hydrogen evolution on mercury are also in good agreement with the assumption of a slow discharge onto free sites on the cathode.

The conception of the evolution of hydrogen on mercury occurring by the Volmer-Heyrovsky mechanism (the slow discharge followed by the electrochemical desorption of hydrogen atoms) is shared at present by most electrochemists. It should be noted, however, that according to Kobozev, who denied the possibility of a slow discharge, the hydrogen overpotential on mercury is caused by an excess energy of free hydrogen atoms escaping from its surface. The emission of free hydrogen atoms is, in Kobozev's opinion, the most effective mecha-

nism of removal of hydrogen atoms from the surface of any metal of low adsorption capacity with respect to hydrogen. Quantitative calculations carried out by Frumkin and his colleagues do not support Kobozev's views. Horuiti believes that the results of investigations of the electrolytic separation of hydrogen isotopes on mercury are in best agreement with the assumption that hydrogen evolution on mercury occurs by the electrochemical desorption mechanism with the slow acception of an electron by an adsorbed ion-molecule H_2^+.

An inference as to the nature of the cathodic hydrogen evolution reaction on other metals of the second electrochemical group—lead, zinc, cadmium and thallium—can be made with lesser certainty. The majority of experimental data (low surface coverage with atomic hydrogen, the value of b close to 0.12, the effect of added substances on the hydrogen overpotential and, finally, small exchange currents close in magnitude to exchange currents on mercury) point to the slow discharge step followed by the electrochemical desorption of hydrogen atoms. A marked increase in the hydrogen overpotential upon transition from a positively to a negatively charged surface is observed on lead, cadmium and thallium and is associated with the rearrangement of the double layer, which results in the desorption of anions and disappearance of their activation effect on the discharge of positive hydroxonium ions H_3O^+ (see Fig. 19.1). If the rate of hydrogen evolution were controlled not by discharge but by some other step, e.g. recombination, the rearrangement of the double-layer structure would not be able to cause such a change in the hydrogen overpotential. Among the metals of the first electrochemical group platinum has been studied most thoroughly, though, because its hydrogen overpotential is highly sensitive to impurities, the reproducibility of the data obtained is not high. Undoubtedly, in the region of positive potentials (not very far from the reversible hydrogen electrode potential) the platinum surface always contains adsorbed hydrogen; this has been established by capacity measurements and by other methods. For example, the amount of adsorbed hydrogen can be found for each potential value with the aid of charging curves, i.e., curves showing the variation of the electrode potential either with the quantity of electricity passed or (at a constant current) with time. In such coulometric determination of the amount of hydrogen (or any other electrochemically active substance) it is necessary that its evolution (or dissolution) proceed with a current efficiency of 100 per cent. All possible secondary reactions—electroreduction or evolution of oxygen, cathodic reduction or anodic oxidation of organic substances and other impurities—must be completely excluded. This can be achieved by two methods. In one of them, the current applied to the cell is so high that it considerably exceeds the limiting currents of reduction and oxidation of impurities; their harmful

effect therefore does not reveal itself. The electrode is charged at a high rate and the charging curve is registered automatically, usually with the aid of an oscillograph. In the other method the deleterious effect of impurities is eliminated either by using an electrode of large surface area (Shlygin), e.g. platinized platinum, or by conducting experiments with a very small volume of the solution (Ershler).

The charging curve for platinum in an acid solution is presented in Fig. 19.7. It consists of sections *1*, *2*, and *3* with different slopes. Section *1*, which originates at the reversible potential of the hydrogen

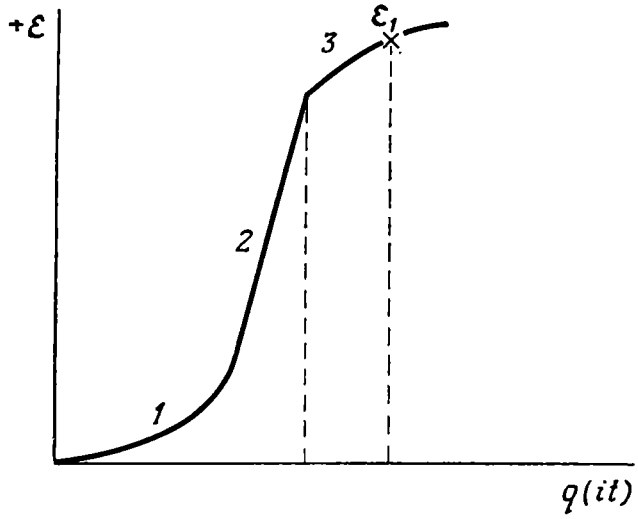


Fig. 19.7. Charging curve for a platinum electrode in an acid solution

electrode and lies in the region of most negative potentials, corresponds to the gradual removal of the hydrogen adsorbed by the electrode surface. Here the current supplied to the electrode is expended on charging the double layer and on ionizing adsorbed hydrogen atoms. The electrical capacity measured by the reciprocal of the slope of the ε vs. q curve

$$C = \frac{1}{\Delta\varepsilon/\Delta q}$$

is therefore high. Section *1* is called the region of the hydrogen sheet. By the moment section *2* is reached the adsorbed hydrogen is completely removed from the electrode surface and the current is now spent exclusively on charging the double layer. Owing to this the capacity falls and section *2*—the region of the ionic double layer—has a steeper slope. At the point where section *3* originates the potential attains a value at which the formation of oxygen becomes possible. This section represents the region of the oxygen sheet and here the current is again consumed to charge the double layer and to effect the electro-

chemical reaction, which increases the capacity (the slope becomes less steep). In this particular case the electrochemical reaction is the anodic formation of oxygen. The amount of adsorbed hydrogen (or oxygen) at each given value of potential can be calculated with the aid of charging curves from the quantity of electricity required for the potential to be shifted from the transition point between sections *2* and *1* (or *2* and *3*, respectively) to the value chosen.

In the region of potentials lying on section *1* near section *2*, when a cathodic current pulse is imposed the hydrogen ions may be discharged to form adsorbed hydrogen atoms. The formation of molecular hydrogen and its evolution as a gas is excluded since the potentials here are more positive than the equilibrium potential of the hydrogen electrode in a given solution.

When experiments are conducted in the atmosphere of an inert gas, then on application of an anodic current pulse the only anodic process will be the ionization of adsorbed hydrogen, which goes into solution. Thus, this region of potentials corresponds only to the discharge (in the case of a cathodic pulse) or ionization step (on application of an anodic pulse), which permits investigating the kinetics of just one step without the complicating effects associated with the recombination or dissociation of hydrogen molecules. By studying the dependence of the double-layer capacity and the ohmic resistance (equivalent to the retardation of the discharge step) on the frequency of the applied current in this region of potentials, Dolin, Ershler, and Frumkin succeeded in measuring the rate of the discharge step directly for the first time. Parallel polarization measurements at small deviations from the equilibrium potential when the overpotential is still linearly dependent on the current density have made it possible to determine the rate of the overall process and to compare it with the rate of the discharge step. It has been established that the discharge step proceeds at a finite rate, which varies with the solution composition simultaneously with the variation of the overall rate of the hydrogen evolution reaction. At the same time the rate of discharge is always higher than the overall rate (27 times higher in solutions of hydrochloric acid and 11 times in solutions of sodium hydroxide). Though the discharge step proceeds at a finite rate, it does not determine the overall rate of hydrogen evolution on a smooth platinum electrode and is not here the limiting or slow step (rds).

According to the most accurate measurement, the value of b for hydrogen evolution on platinum is about 0.03, which also testifies against the slow occurrence of a purely electrochemical step since the value of the transfer coefficient α cannot exceed unity. On evolution of hydrogen on platinum the stoichiometric number ν is equal to unity. This value is in accord with the theory of slow recombination. That the hydrogen overpotential on platinum is independent of pH also points to the greater probability of the slow recombination.

Finally, for platinum a limiting current of nondiffusional origin is observed, which is possible only when the recombination step is slow.

This conclusion seems to be in contradiction with the shape of a polarization curve obtained for hydrogen evolution from acid solutions. As seen from Fig. 19.1, the ε vs. log i curve for platinum consists of two portions with different values of the constants a and b. In the lower portion the coefficient b is equal to 0.03, and in the upper one it is about 0.12. But, in contrast to the similar curve for lead, the sharp change of the overpotential cannot be ascribed here to the recharging of the surface since the null point of platinum ($_{Pt}\varepsilon_N$ = = 0.2 V) is more positive than the equilibrium potential of the hydrogen electrode. It is supposed that in the region of the lower branch of the polarization curve the source of hydrogen is hydroxonium ions, the discharge of which occurs more readily than the recombination of hydrogen atoms. In the region of the upper branch it is water molecules that are discharged, which requires a larger amount of activation energy, and in this case the discharge step runs slow. Transition from the lower to the upper branch is observed when the limiting current for hydroxonium ions is reached.

Thus, most of the experimental data on the cathodic evolution of hydrogen on platinum indicate that the most probable cause for the appearance of an overpotential is the slow recombination step. At the same time there are grounds for stating that when platinum is poisoned (or when its potential deviates considerably from the equilibrium value), the mechanism of electrolytic hydrogen evolution may change and the discharge or electrochemical desorption may become the slow step. Considering that the surface of a smooth platinum electrode is inhomogeneous it is not improbable that the hydrogen evolution reaction proceeds differently on its different areas. On spongy or platinized platinum, because of its high catalytic activity the deviation of the potential observed when the current is switched on is probably caused by the slow removal of molecular hydrogen from the solution adjacent to the electrode.

Palladium resembles platinum in many respects in its behaviour during the electrochemical evolution of hydrogen. Experimental data on exchange currents and on the slope of Tafel lines point to the slow recombination step as a probable cause for the appearance of the hydrogen overpotential. That the slow recombination step on palladium electrodes is possible was proved by Kobozev and Monblanova (1935). They used a thin palladium membrane one side of which, the polarization side, was always in contact with the solution and could be polarized by an external current, and the other, the diffusion side, was in contact with the gas phase or solution (Fig. 19.8). When a cathodic current is applied to the polarization side of the membrane and the potential is displaced in the negative

direction, hydrogen evolves first only on the polarization side and then on the diffusion side as well. Simultaneously the potential of the diffusion side also becomes more negative. Such a transfer of hydrogen and of the overpotential from the polarization to the diffusion side is possible only in those cases where the atomic hydrogen formed during discharge has no time to leave the electrode surface. Its concentration increases as compared with the equilibrium value and it begins to permeate into the palladium electrode, reaching the diffusion side of the membrane. The appearance of excess hydrogen on the diffusion side shifts its potential in the negative direction, which also testifies to the slow recombination. According to Frumkin, however, the hydrogen overpotential on palladium cannot be attributed to the slow recombination alone. If the membrane is polarized to a constant potential by a small current and the current is then switched off, different potential-decay curves will be obtained for the two sides of the membrane. On the polarization side, immediately after the current is switched off the overpotential first falls abruptly and then decreases much slower. On the diffusion side, only the second section appears, i.e., after the current is switched off the potential is gradually displaced to its equilibrium value in a given solution. The rapid fall of the overpotential is ascribed to the slow discharge, and the gradual fall to the removal of excess hydrogen.

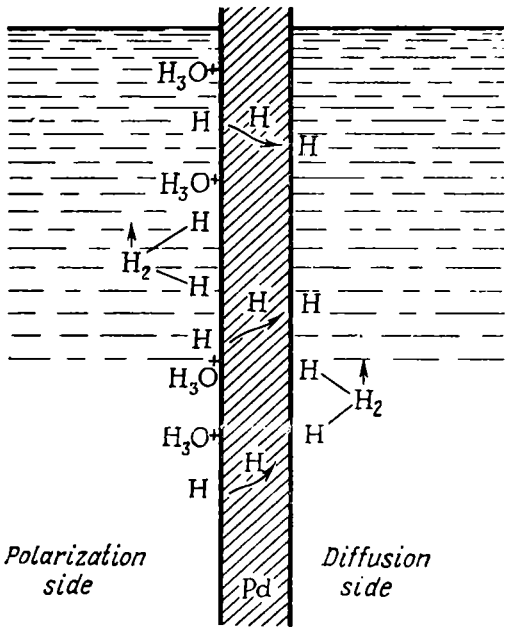


Fig. 19.8. Transfer of hydrogen from the polarization to the diffusion side of a membrane

Still more obscure is the mechanism of hydrogen evolution on metals of the iron group. It has been found that under the conditions of cathodic polarization an excess amount of adsorbed hydrogen accumulates on the surface of these metals. This follows, for example, from experiments on electrodiffusion of hydrogen through iron, which have yielded almost the same results as those obtained for palladium. The slope of Tafel constant b for metals of the iron group is close to 0.12, which is indicative of the slow discharge step. The same value however can also be obtained from the theory of slow recombination at the

coverage of the surface with adsorbed hydrogen atoms observed on metals of the iron group. For hydrogen evolution on nickel it has been found that the overpotential depends on the pH value. All attempts to explain the character of this dependence by the slow occurrence of the discharge or the recombination step have failed. The higher probability of the recombination step running slow is borne out by data on the hydrogen isotopic separation factor and also by the tendency toward the appearance of a nondiffusional limiting current in nickel electrodes. For metals of this group the most likely assumption is that several steps—discharge, recombination and, perhaps, electrochemical desorption—proceed at almost the same rate. Depending on the conditions any one of these steps can be rate determining, and thus the hydrogen evolution reaction will be forced to proceed by one of the mechanisms considered above. Here, as with metals of the platinum group, the nature of the hydrogen overpotential may be different on different sites of the cathode.

CHAPTER 20

The Kinetics of the Oxygen Evolution Reaction

20.1. GENERAL DESCRIPTION OF THE PROCESS

The oxygen evolution reaction may proceed by different paths depending on the composition of the solution subjected to electrolysis. In the electrolysis of alkaline solutions the most probable source of anodic oxygen is hydroxyl ions. The overall reaction in the anodic evolution of oxygen in alkaline solutions is the discharge of hydroxyl ions according to

$$4OH^- = O_2 + 2H_2O + 4e \qquad (20.1)$$

In acid solutions, in which the concentration of OH^- ions is too low for the anodic evolution of oxygen to proceed at the required rate, water molecules are discharged

$$2H_2O = O_2 + 4H^+ + 4e \qquad (20.2)$$

In neutral salt solutions oxygen can be produced by the discharge of either hydroxyl ions or water molecules. Of these two reactions the one that consumes less energy under given conditions will predominate. In concentrated solutions of oxygen-containing acids the oxygen evolution reaction may involve anions of an acid, at least at high current densities. The existence of this mechanism was proved by Gerovich and coworkers (1957) in experiments on the electrolysis of concentrated solutions of perchloric and sulphuric acids tagged with the heavy oxygen isotope ^{18}O. At high current densities the oxygen evolved on platinum contains this isotope. Since the isotopic exchange of oxygen between acid anions and water molecules in solution is practically impossible, the appearance of the heavy oxygen isotope in the evolving gas should wholly be ascribed to the participation of anions in the anodic formation of oxygen. In the case of sulphuric acid, oxygen evolution may take place by the direct participation of anions. Oxygen evolves here as a result of the discharge of sulphate ions, e.g., according to the reaction

$$2SO_4^{2-} = 2SO_3 + O_2 + 4e \qquad (20.3)$$

followed by the recovery of SO_4^{2-} ions

$$2SO_3 + 2H_2O = 2SO_4^{2-} + 4H^+ \qquad (20.4)$$

In the case of perchloric acid, considering that perchlorate ions are incapable of discharging, other factors are responsible for the appearance of the isotope ^{18}O in the gas phase. It is possible that here isotopic exchange takes place between the oxygen-tagged adsorbed anions and the surface oxides of platinum, these oxides decomposing to evolve oxygen containing the heavy isotope. This mechanism is also possible in the electrolysis of sulphuric acid solutions. In either case, however, the overall anodic oxygen evolution reaction proceeds according to scheme (20.2).

Oxygen is always evolved at potentials more positive than the potential of the reversible oxygen electrode under given conditions. Here the difference between the electrode potential under an external current and the equilibrium potential of an oxygen electrode is identified with activation polarization and is called the oxygen overpotential:

$$\eta_{Ox} = \varepsilon_i - \varepsilon_r \qquad (20.5)$$

Further in the text the oxygen overpotential will be denoted by η, the subscript being omitted.

20.2. EXPERIMENTAL DATA ON OXYGEN OVERPOTENTIAL

Theoretically and practically, the anodic evolution of oxygen is nearly as important as the cathodic hydrogen-evolution reaction. The two reactions constitute the process of electrolytic decomposition of water:

$$2H_2O = 2H_2 + O_2 \qquad (20.6)$$

The oxygen overpotential represents a considerable fraction of the total overpotential in a cell for electrolysis of water and affects the consumption of electric power in the industrial electrolytic production of hydrogen and oxygen. The oxygen evolution reaction plays an important role in practically all anodic processes in the electrolysis of aqueous solutions and, primarily, in electrolytic reactions of oxidation of inorganic and organic substances. The mechanism of the oxygen evolution reaction however has not yet been fully clarified.

The lack of reliable data on oxygen overpotential is due to the complexity of the process of anodic oxygen evolution and by the inevitable occurrence of side and secondary reactions. It should first be recalled that it is extremely difficult to set up a reversible oxygen electrode under experimental conditions and hence the quantity ε_r occurring in Eq. (20.5) is not determined by experiment. It is usually calculated theoretically. For gaseous oxygen to be evolved from acidic solutions it is necessary that the anode potential be more positive than the equilibrium potential of the oxygen elec-

trode (+1.23 V at $a_{H^+} = 1$ and 25°C) by the value of oxygen overpotential corresponding to a given current density. But even before this potential is reached most metals become thermodynamically unstable and, instead of the oxygen evolution reaction, there occurs the process of their anodic dissolution or oxidation. The kinetics of oxygen evolution from acid mediums can therefore be studied only by using metals of the platinum group and gold (the standard potentials of which are more positive than the potential of an oxygen electrode) and also some other metals protected against dissolution in acid solutions by stable surface oxides. In alkaline solutions, in which the equilibrium oxygen potential is less positive (at $a_{OH^-} = 1$ and 25°C it is about + 0.41 V), metals of the iron group, cadmium and some other metals are also used as the anode. It has been found that under the conditions of oxygen evolution the surface of all metals, including platinum and gold, is oxidized to a greater or lesser degree and therefore oxygen usually evolves not on the metal itself but on its oxides.

The oxygen overpotential has been found to vary with time at a given current density. As a rule, it increases with time, gradually for some metals (iron, platinum) and jumpwise for others (lead, copper). The overpotential is commonly taken to mean its steady-state value. It evidently corresponds to the evolution of oxygen at the surface of an oxide stable in a given range of potentials. Curves of ε vs. log i or η vs. log i obtained for oxygen evolution often show one or more inflections indicating abrupt changes in the kinetics of the process. Examples of such curves pertaining to oxygen evolution on lead and nickel anodes are shown in Fig. 20.1. On these curves, just as in the case of curves obtained for other electrodes, one or more sections can still be picked out where the overpotential is linearly dependent on the logarithm of the current density and obeys Tafel's equation:

$$\eta = a + b \log i$$

The constants a and b depend on the electrode material, temperature, the solution composition and current density. This complicates the comparison of metals by their oxygen overpotential. The bulk of experimental data indicates that in the region of mean current densities (of the order of 10^{-3} A/cm^2) the overpotential associated with the evolution of oxygen from alkaline solutions increases in approximately the following sequence:

Co, Fe, Ni, Cd, Pb, Pd, Au, Pt

The dependence of the overpotential on the electrode material is seen here quite distinctly. For example, at one and the same current density equal to 1 mA/cm^2 the oxygen overpotential increases by more than 0.7 V with a change from cobalt anodes to platinum ones.

Some data illustrating the dependence of the oxygen overpotential on the type of the metal are presented in Table 20.1.

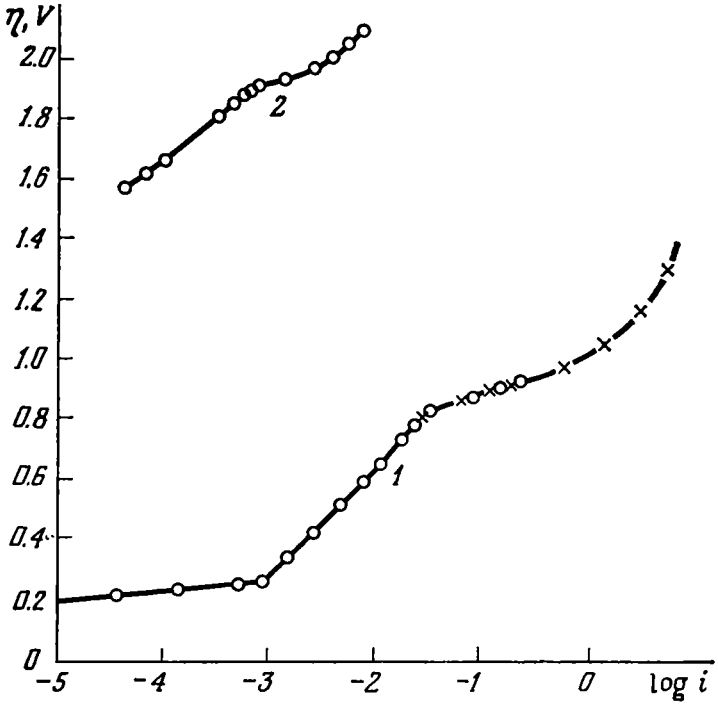


Fig. 20.1. Polarization curves for oxygen evolution on nickel (*1*) and lead (*2*)

The relation between the oxygen overpotential and the solution composition and temperature has been systematically studied but

TABLE 20.1

The Effect of Electrode Material and Solution Composition on Oxygen Overpotential

Metal	Solution	t, °C	Current density, A/cm²	$\frac{b}{2.303}$	a
Pt	0.005-0.05N H_2SO_4	25	10^{-7}-10^{-4}	$3/2RT/F$	0.95
Pt	0.1N H_2SO_4	35	10^{-7}-10^{-2}	$2RT/F$	1.08
Pt	0.1N NaOH	25	—	RT/F	—
Au	0.1-1.0N H_2SO_4	25	3×10^{-5}-10^{-2}	$3/4RT/F$	0.99
Au	0.1N NaOH	25	—	RT/F	—
Pb	3.8N H_2SO_4	30	—	$2RT/F$	1.10
Pt, PbO_2 (α)	4.4N H_2SO_4	31.8	10^{-4}-2×10^{-3}	$3/4RT/F$	0.72
Pt, PbO_2 (β)	4.4N H_2SO_4	31.8	7×10^{-5}-2×10^{-3}	$2RT/F$	1.17
Ni	7.5N KOH	25	5×10^{-6}-10^{-3}	$1/2RT/F$	0.35
Ni	7.5N KOH	25	10^{-3}-5×10^{-2}	$3RT/F$	1.30
Ni	7.5N KOH	25	5×10^{-2}-3×10^{-1}	RT/F	1.08
Fe	pH 2 —	5	3×10^{-6}-10^{-4}	$1/2RT/F$	0.66

for a limited number of metals. According to the data obtained by Izgaryshev and coworkers (1953) the increase of the concentration of sulphuric acid from 36 to 1759 g/litre considerably increases the oxygen overpotential on platinum. For instance, at 20°C and a current density of 1×10^{-2} A/cm^2 the overpotential increases by more than 1V. A rise in temperature lowers the overpotential over the entire concentration range indicated. Here not only the constant a decreases but also the slope b of the Tafel line. According to the measurements carried out by Bowden (1930), who used dilute solutions of sulphuric acid, the rise of temperature lowers the oxygen overpotential on platinum owing to the decrease of a; conversely, the slope of semilogarithmic straight lines increases. At a specified temperature the slope is a function of the acid concentration, increasing parallel with it. In concentrated solutions of sulphuric acid the slope reaches 0.36. The oxygen overpotential is also affected by the presence in solution of foreign cations and fluorides, the addition of which increases the oxygen overpotential. Conversely, the overpotential at a gold electrode depends neither on the solution pH nor on the addition of extraneous salts.

At potentials close to the zero-charge potential of oxidized lead the oxygen overpotential remains almost constant with varying sulphuric acid concentration. At small positive charges on the surface of a lead anode the overpotential is found to fall slightly with increasing acid concentration; when the positive charge increases, the opposite effect is observed.

The behaviour of nickel electrodes during oxygen evolution from alkaline solutions largely depends on the degree of their oxidation. The oxygen overpotential measured on oxidized nickel electrodes is given by the equation

$$\eta = a + b_1 \log i - b_2 \log [OH^-] \qquad (20.7)$$

where b_1 and b_2 may assume values of 0.027-0.088 and 0.046-0.086, respectively, depending on the degree of oxidation.

20.3. THE POSSIBLE MECHANISM OF THE ANODIC OXYGEN EVOLUTION REACTION

Elucidation of the kinetic mechanism of the oxygen evolution reaction at an anode is a formidable task, associated not only with considerable experimental difficulties but also with the great number of theoretically possible reaction paths. The electrolytic oxygen evolution reaction involves not two, as in hydrogen evolution, but four electrons, no matter whether it takes place in acidic, neutral or alkaline solutions. This leads to the appearance of several electrochemical steps, each of which can determine the rate of the overall anodic process. Besides, in oxygen evolution one has to reckon with the

possibility of the recombination and electrochemical-desorption steps proceeding at a slow rate. Finally, since the evolution of oxygen usually occurs on the surface of a metal the degree of oxidation of which depends on the potential and electrolysis time, the formation and decomposition of oxides may also affect the kinetics of this process. There exists an opinion first expressed by Foerster (1909), according to which the anodic evolution of oxygen in all cases proceeds only via the formation of intermediate unstable oxides. The transformation of these into stable oxides (or to the state of the initial metal with the simultaneous loss of oxygen evolved as a gas) controls the kinetics of the overall electrode reaction. Thus, the appearance of an oxygen overpotentials is due to a number of factors and may be associated with the slow rate of one of the following steps: discharge of hydroxyl ions or water molecules; recombination of oxygen atoms; electrochemical desorption of hydroxyl radicals OH; formation and decomposition of unstable intermediate oxides of the electrode metal.

Various kinetic mechanisms of the oxygen evolution reaction have been proposed, based on different assumptions as to the probable nature of the slowest step in the overall process. Some of these reaction mechanisms are given in Table 20.2. They all refer to the case of oxygen evolution from alkaline solutions and therefore the first step in each mechanism is the discharge of hydroxyl ions. These ions are discharged to yield hydroxyl radicals (mechanisms I, II and IV) or a surface hydrated oxide of the anode metal (mechanism III). Table 20.2 does not cover all the possible paths of the oxygen evolu-

TABLE 20.2

Some Possible Mechanisms of Oxygen Evolution from Alkaline Solutions

I	II
1. $2OH^- = 2OH + 2e$ 2. $2OH + 2OH^- = 2O^- + 2H_2O$ 3. $2O^- = 2O + 2e$ 4. $2O = O_2$	1. $2OH^- = 2OH + 2e$ 2. $2OH + 2OH^- = 2O^- + 2H_2O$ 3. $2O^- + 2MO_x = 2MO_{x+1} + 2e$ 4. $2MO_{x+1} = 2MO_x + O_2$
III	**IV**
1. $4OH^- + M = 4MOH + 4e$ 2. $4MOH = 2MO + 2M + 2H_2O$ 3. $2MO = 2M + O_2$	1. $2OH^- = 2OH + 2e$ 2. $2OH + 2OH^- = 2H_2O_2^-$ 3. $2H_2O_2^- = O_2^{2-} + 2H_2O$ 4. $O_2^{2-} = O_2 + 2e$

tion reaction. For instance the first step of the process may be visualized in a different way from that given in the table. It may be assumed, for example, that hydroxyl ions are discharged to yield not hydroxyl radicals or hydrated oxides but atomic oxygen or an unstable surface oxide according to the equations

$$2OH^- = O + H_2O + 2e \tag{20.8}$$

and

$$2OH^- + MO_x = MO_{x+1} + H_2O + 2e \tag{20.9}$$

respectively.

In spite of its incompleteness, Table 20.2 correctly reflects the basic conceptions of possible steps involved in the electrolytic oxygen evolution reaction. According to mechanism I molecular oxygen results from the recombination of its oxygen atoms formed in the discharge of univalent oxygen ions O^-, and according to mechanism II, from the decomposition of a higher unstable oxide MO_{x+1} formed from a lower stable oxide MO_x after the ions O^- are discharged on it. Mechanism III excludes the participation of any charged particles, except hydroxyl ions, in the electrode reaction. Here the oxygen evolution reaction involves intermediate steps—the formation and decomposition of oxide hydrates and metal oxides. In mechanism IV the direct source of oxygen is its ion-molecules O_2^{2-} formed from hydrated ions $O_2^{2-} \cdot 2H_2O$ after the water molecules are lost. These hydrated oxygen ions may be regarded as negatively charged molecules of hydrogen peroxide $H_2O_2^-$ which serve as an intermediate link in the anodic oxygen evolution process.

Any step in each of these mechanisms may run slow and determine the rate of the overall reaction. To make a choice from these theoretically possible cases and to find out the actual cause of the oxygen overpotential one should resort to criteria following from the general theory of electrode kinetics. One such criterion may be the slope of semilogarithmic straight lines. As follows from Table 20.1, the slope b in oxygen evolution varies within wide limits, assuming the following values depending on the anode material and solution composition:

$$1/2b^0,\ 3/4b^0,\ b^0,\ 3/2b^0,\ 2b^0 \text{ and } 3b^0 \left(b^0 = 2.303\frac{RT}{F}\right)$$

If, by analogy with hydrogen evolution, one assumes that the transfer coefficient α is close to 0.5, then the slow discharge of hydroxyl ions (steps I-1, II-1, III-1, and IV-1) must give a slope equal to $2b^0$. The slow occurrence of any other step will result in a smaller slope. For instance, if the rate of the overall process is limited by step IV-2, the slope must then be equal to b^0, and if steps III-2 and III-3 are rate determining, we have $^1/_2\ b^0$ and $^1/_4\ b^0$, respectively.

The values of b (see Table 20.1 and Fig. 20.1) found in experimental studies of oxygen evolution from acid solutions on lead anodes and from alkaline solutions on nickel coincide with the value $b = 2b^0$ (0.12 at room temperature). It may therefore be supposed that the kinetics of the overall process is determined by the rate of purely electrochemical steps: the discharge of water molecules in acid solutions and of hydroxyl ions in alkaline solutions. The nature of the effect of the solution composition on oxygen overpotential in the two cases considered is also in accord with Frumkin's theory of slow discharge.

At small current densities the evolution of oxygen on nickel (see Fig. 20.1, curve *1*, lower section) is characterized by a slope corresponding to $b = b^0$, which is hardly in accord with the assumption of the slow discharge of hydroxyl ions. On this section of the polarization curve the kinetics of the process is determined by steps I-3, II-3, or by the interaction of atomic oxygen, formed according to reaction (20.8), with a nickel oxide:

$$O + Ni_2O_3 = Ni_2O_4 = 2NiO_2 \qquad (20.10)$$

In the case of oxygen evolution from an alkaline solution on platinum or gold the most probable rate-determining step must be step IV-2.

It should however be borne in mind that all these inferences are but assumptions. The slope b cannot be taken as a sufficient criterion to decide in favour of one or the other mechanism. Moreover, in such a complex process as the electrochemical evolution of oxygen there is always a possibility of the parallel occurrence of several steps with similar rate constants. For instance, experimental data on oxygen evolution at lead agree best with the slow-discharge theory, but the possibility of slow recombination of oxygen atoms is not excluded. This is evidenced by the current-density variation of the concentration of atomic oxygen on the surface of the lead elecrode and also by the change of the rate of diffusion of oxygen atoms through lead dioxide. Another step, which runs concomitantly with the discharge of hydroxyl ions and oxygen evolution, is the formation of oxides, whose composition depends on the current density and electrode potential. Thus, a theory of oxygen overpotential cannot be worked out without taking into account the oxidation of the anode surface. The formation of oxides on the anode sharply changes the kinetics of oxygen evolution and the oxygen overpotential. The latter not only varies widely in going from a pure metal surface to an oxidized one but is also determined by the nature of the oxides themselves. Thus, from the data of Table 20.1 it follows that when one changes from the β- to the α-modification of lead dioxide the Tafel constant a falls by more than 0.4V and the slope b decreases from $2b^0$ to $^3/_4\ b^0$; this points to a change in the kinetics of the reaction mechanism.

Similar results have been obtained in studies of oxygen evolution at nickel; it was found that the overpotential sharply rises when Ni_2O_3 is converted to Ni_2O_4. The transition from the lower portion of curve *1* in Fig. 20.1 to the upper one should be attributed to the increase of the content of the higher nickel oxide in the surface layer. Thus, the overpotential of oxygen and the kinetics of its evolution may vary depending on the chemical composition of the surface

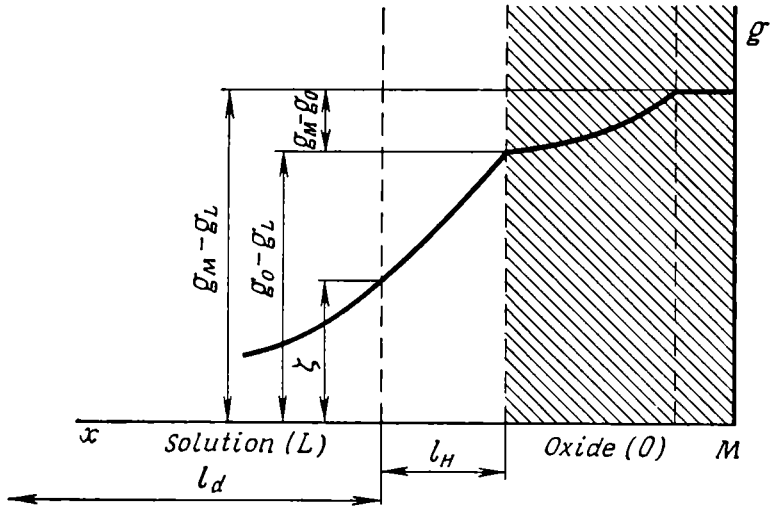


Fig. 20.2. Probable distribution of the potential drop in the electric double layer at the oxidized metal-solution interface:

$g_M - g_0$ = potential drop in the metal-oxide layer; $g_0 - g_L$ = potential drop between the oxide surface and the bulk of the solution; $g_M - g_L$ = total potential drop of the metal-solution potential; l_H and l_d are the thicknesses of the Helmholtz and diffuse parts of the double layer, respectively

oxide; if the composition is constant throughout the process, they may vary according to the ratio of different crystallochemical modifications in the oxide. This also affects polarization curves.

The appearance of an oxide on the metal surface alters the double-layer structure. In this case the double layer can no longer be represented by the simple Stern model, which was used in developing the theory of hydrogen overpotential. According to Göhr and Lange (1958), the electric double layer in the oxygen evolution reaction should be pictured as shown in Fig. 20.2. To the potential drop in the Helmholtz and diffuse parts of the double layer, included in the Stern model, is added the potential drop in the oxide layer. The latter term is often disregarded since the surface metal oxides, on which oxygen evolution is studied, possess high electronic conductance. What is more important is that the Helmholtz region of the double layer begins in this case not from the bare surface of the metal but from the surface of its oxide, whose properties are different from those of the metal. In particular, the oxidation of the metal shifts

the charge-free potential of the electrode surface to the positive side. For example, the null point of pure lead is -0.7 V and that of lead covered with its dioxide is about $+1.8$ V. The appearance of a horizontal section on curve *2* (Fig. 20.1) is probably due precisely to the transition through the null point of Pb, PbO_2 and to the corresponding change in the rate of discharge of water molecules. The formation of platinum oxides and the related change of its null point and hence of the charge on the surface may be regarded as one of the causes for the appearance of inflections on polarization curves corresponding to oxygen evolution on platinum. The possibility of the anode surface being recharged during the formation of oxides (or during the change of their composition) should be taken into account when examining data on the effect of the solution pH and also of extraneous ions and surface-active substances on the kinetics of oxygen evolution; it should also be reckoned with in studying the anodic oxidation of inorganic and organic substances. In this case experimental data can hardly be interpreted in the same way as was done in studying the same effects on pure metals, i.e., only by assuming that the double-layer structure is changed under the influence of these substances. A change in the solution composition may affect the kinetics of oxygen evolution and the composition and properties of the oxides formed. This in turn may change essentially both the value and nature of oxygen overpotential. Perhaps precisely these effects are responsible for the buildup of the oxygen overpotential observed on lead anodes as the sulphuric acid concentration increases. If the only result of an increase in the sulphuric acid concentration is the rearrangement of the double layer associated with the increased electrostatic adsorption of sulphate ions, the overpotential should be expected to fall, which has actually been observed in dilute solutions. The opposite effect—the buildup of overpotential detected in more concentrated solutions of sulphuric acid—must be caused by other factors and, primarily, by a change in the composition of the surface oxide layer. It is possible that the increase of the sulphuric acid concentration increases the relative content of the β-modification of lead dioxide, on which the oxygen overpotential is higher than on the α-modification.

CHAPTER 21

The Kinetics of Electrochemical Reduction and Oxidation

21.1. GENERAL DESCRIPTION OF REDOX REACTIONS

Electrochemical reduction and oxidation reactions cover a wide range of processes, from the simplest ion-recharge reaction to complex transformations forming the basis of organic electrosynthesis. Electrochemical reduction and oxidation reactions are used in industrial production of hydrogen peroxide, manganese dioxide, potassium permanganate, sodium hydrosulphite, *p*-aminophenol, adiponitrile, salicylaldehyde and a number of other compounds. These processes lie at the basis of the operation of most chemical sources of current.

Polarization in redox reactions may be defined as the difference between the electrode potential in the presence of an external current and its equilibrium value:

$$\eta_R = {}_R\varepsilon_i - {}_R\varepsilon_r \qquad (21.1)$$

When determining the redox polarization from Eq. (21.1) the following points must be taken into account.

In reduction-oxidation processes the diffusion overpotential is usually high and often constitutes a considerable, and sometimes even the major, part of the total deviation of the electrode potential. As the role of concentration overpotential in redox processes has already been discussed, we will be concerned here only with the chemical and electrochemical overpotentials. It is assumed that the diffusion overpotential is either taken into account or eliminated.

For most reduction-oxidation reactions (particularly those with the participation of complex organic substances) the equilibrium potential is not directly measurable. Unlike the oxygen electrode potential, it does not always lend itself to calculation either. Therefore, to characterize the kinetics of redox reactions the value of electrode potential set up by an external current is often used instead of the polarization.

Any electrochemical reduction (or oxidation) process taking place in aqueous solution is accompanied by a secondary hydrogen (or oxygen) evolution reaction. The distribution of current between these two competing reactions depends on the corresponding potential at a given current density. Therefore, apart from the magnitude of polarization, one also makes use of the so-called depolarization

$\Delta\varepsilon_R$ to describe a redox reaction. This quantity is defined as the difference between the potential of the corresponding redox process and the potential of hydrogen (oxygen) evolution under comparable conditions and at the same current density:

$$\Delta_H\varepsilon_R = {}_R\varepsilon_i - {}_H\varepsilon_i \tag{21.2}$$

or

$$\Delta_O\varepsilon_R = {}_R\varepsilon_i - {}_O\varepsilon_i \tag{21.3}$$

The concept of depolarization was first introduced in connection with the fact that electroreduction was thought to be unfeasible in the absence of active hydrogen just as electrolytic oxidation was considered impossible without active oxygen. The binding of these active forms of hydrogen and oxygen with the aid of a suitable substance would inevitably decrease, the absolute value of potential under such conditions, i.e., cause depolarization. Substances capable of binding hydrogen (or oxygen) were termed depolarizers. This concept of the nature of redox reactions is now obsolete and has already been abandoned by most scientists, and the term "depolarization" has lost its original meaning. Reduction and oxidation reactions are known at present, which proceed at potentials higher than the potentials of hydrogen or oxygen evolution, i.e., the "depolarization" may be not only positive but negative. The following reaction may serve as an example:

$$2RCOO^- = R - R + 2CO_2 + 2e$$

Here the anodic oxidation of anions of carbonic acids yields dimerization products. These reactions were discovered in the middle of the nineteenth century and form the basis of Kolbe synthesis. They enable complex organic molecules of desired structure to be produced by electrolysis of solutions containing salts of corresponding carbonic acids. In most cases the Kolbe synthesis proceeds at potentials more positive than the oxygen-evolution potential at a given electrode. Thus, in this case the change from the oxygen-evolution reaction to the electrooxidation of an organic substance is accompanied not by a fall but an increase in the electrode potential, and no depolarization effect is observed. Nonetheless comparison of the potentials ${}_R\varepsilon_i$ and ${}_H\varepsilon_i$ or ${}_R\varepsilon_i$ and ${}_O\varepsilon_i$ as well as determination of the depolarization $\Delta\varepsilon_R$ is useful in redox-reaction studies.

Apart from the steps taking place at the electrode-electrolyte interface, purely electrochemical transformations occurring in the electrolyte may also be important in an electrolytic reduction or oxidation reaction. Consequently, the volume of the electrolyte must also be regarded as a parameter to be taken into account. Therefore, apart from the current density i, space current density j is also used to characterize the conditions under which redox reactions occur; the space current density is the current referred to a unit volume (usually one litre) of the solution.

21.2. EXPERIMENTAL DATA ON THE KINETICS OF ELECTROCHEMICAL REDUCTION AND OXIDATION REACTIONS

A great number of inorganic and organic substances have been studied to determine the redox polarization under different electrolysis conditions. Experiments have been carried out to study the polarization on recharging of ions of iron, manganese, thallium, cerium, vanadium, tin, gold, platinum, titanium, tungsten, and molybdenum, and complex ions of iron $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, manganese $Mn(CN)_6^{4-}$, $Mn(CN)_6^{3-}$ and MnO_4^{2-}, MnO_4^- and of some other metals. Polarization has also been investigated for the oxidation and reduction of quinones and hydroquinones, nitro compounds, ketones and aldehydes, organic unsaturated compounds, etc.

21.2.1. POLARIZATION AND THE PROPERTIES OF REACTING SUBSTANCES

Electrode polarization in reduction-oxidation reactions is the stronger, the greater are the changes in the structure and composition of particles occurring during a reduction or oxidation reaction. For example, in the following ion-recharge processes:

$$Fe^{3+} + e = Fe^{2+}$$
$$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$$
$$MnO_4^- + e = MnO_4^{2-}$$

where the changes reduce to the gain or loss of one electron, the activation polarization is negligibly small. Its value under comparable conditions will be higher if two electrons instead of one participate in the reaction, e.g.,

$$Tl^{3+} + 2e = Tl^+$$
$$Sn^{4+} + 2e = Sn^{2+}$$

If the composition of the reacting particles, as well as the number of charges, changes in the course of a redox reaction, the activation polarization continues to increase. Examples are the reactions of recharge of cerium and vanadium ions:

$$CeO^{2+} + 2H^+ + e = Ce^{3+} + H_2O$$
$$VO_3^- + 4H^+ + e = VO^{2+} + 2H_2O$$

and the electroreduction of nitrobenzene

$$C_6H_5NO_2 + 6H^+ + 6e = C_6HNH_2 + 2H_2O$$

and of acetone

$$CH_3COCH_3 + 2H^+ + 2e = CH_3CHOHCH_3$$

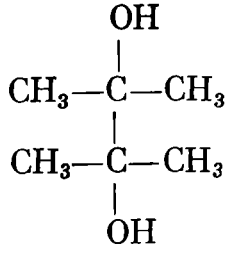
How readily the active group of an organic compound (e.g., the carbonyl or nitro group) will reduce depends on the nature of the substituents introduced into the initial molecule. Reduction proceeds with less polarization if electronegative substituents of the hydroxyl or chlorine type are added. Conversely, the reaction occurs with difficulty if electropositive groups, e.g., the methyl group, are introduced (the rule of electronegativity formulated by Shikata and Tachi, 1932).

The course of the reduction is affected not only by the type of the substituent but also by its position in the molecule to be reduced. For instance, the reduction potential of nitro compounds has been found to shift most strongly to the positive side on addition of the same substituents at the ortho-position. All these data on the effect of the structure on the reduction process refer to mercury electrodes and have been obtained by polarographic methods. When a mercury dropping electrode is used, the electroreduction of organic substances proceeds with more ease with increasing dipole moments of these substances.

21.2.2. THE EFFECT OF THE ELECTRODE MATERIAL AND THE ELECTRODE POTENTIAL

The nature of an electrode and its surface area play an important role in the kinetics of electrochemical reduction and oxidation reactions; their effect is manifested especially distinctly in complex redox reactions. It has been found, for example, that the reduction of nitric acid on spongy copper yields practically only ammonia and when amalgamated lead is used as the electrode hydroxylamine is predominantly formed. At a current density of 0.24 A/cm^2 on a copper cathode 98.5 per cent of current is used for the formation of ammonia and only 1.5 per cent is spent on producing hydroxylamine. Conversely, when amalgamated lead is used, the current yield of ammonia is only 30 per cent and that of hydroxylamine amounts to 70 per cent.

Another example illustrating the effect of the electrode material on electroreduction is the reduction of acetone. This reaction produces two principal end products—isopropyl alcohol $CH_3CHOHCH_3$ and pinacol



When a solution of acetone in sulphuric acid is subjected to electrolysis, the reduction process occurs at a potential of about —0.8 V on the hydrogen scale; the highest current yield of pinacol is obtained on lead and zinc, while on copper, nickel and silver the current is almost completely expended on producing isopropyl alcohol.

The effect of the electrode material is sometimes ascribed only to the hydrogen overpotential arising at it. Indeed, metals of high hydrogen overpotential often promote reduction. Besides, on such electrodes the potentials at which difficultly reducible substances can be reduced are attained more easily. In a general case, however, no direct connection exists between the hydrogen overpotential on the electrode material (or the cathode potential) and its reducing action. Moreover, some substances have been found to reduce more readily on cathodes of low overpotential than on those of high overpotential, where they are altogether unreducible sometimes. Such selective electroreduction is widespread among organic substances (Antropov, 1951). Examples of selective reduction are given in Table 21.1. Isolated unsaturated bonds in organic compounds of the aliphatic series and double bonds in the benzene ring are predominantly reduced on cathodes of low overpotential—platinum and nickel (particularly in the form of black and sponge). At the same time these bonds are practically never hydrogenated on cathodes having a high hydrogen overpotential such as mercury or lead. Conversely, polar groups—the carbonyl and carboxyl groups—are reducible at cathodes of high hydrogen overpotential and remain intact on those having a low overpotential. Exceptions are nitro and nitroso groups and also conjugate double and triple bonds; they can be reduced practically on any cathode.

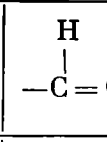
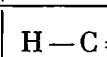
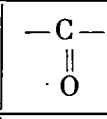
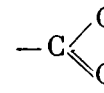
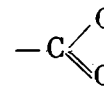
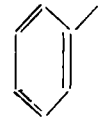
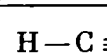
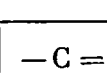
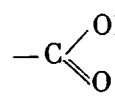
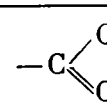
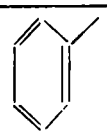
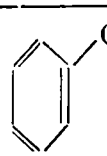
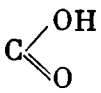
The change of the electrode potential during electrolysis affects electroreduction. While being shifted to the negative side, the cathode potential attains such a value at which reduction becomes possible[1]. With increasing negative value of the potential the rate of reduction increases until it reaches a certain limiting value. At sufficiently negative potentials the reduction rate diminishes and the corresponding current density falls. This is most distinctly manifested in the reduction of anions, in particular, in the reduction of persulphate ions (Fig. 21.1).

The decrease of the reduction rate is the more pronounced, the lower the concentration of extraneous ions; the current begins to fall near the null point of mercury. When electrodes other than mercury are used (platinum, copper, lead or cadmium), the i vs. ε curves are of the same shape, the fall in the current being usually observed

[1] The reduction of a number of substances containing, for example, a nitro group, begins even at a potential which practically does not differ from the steady-state value, which is set up in the presence of such a substance without application of an external current.

TABLE 21.1

Selective Reduction of Organic Compounds on Different Cathodes

Compound	Reducible group	Reducing action		Principal reduction products
		Pt, Ni	Hg, Pb	
Acetaldehyde		—	+	Ethyl alcohol
Acetylene		+	—	Ethylene, ethane
Acetone		—	+	Isopropyl alcohol, pinacol
Benzaldehyde		—	+	Benzyl alcohol
Benzoic acid		—	+	Benzaldehyde, benzyl alcohol
Benzoic acid		+	—	Cyclohexane carboxylic acid
Vinylacetylene		+	—	Divinyl
Oleic acid		+	—	Stearic acid
Salicylaldehyde		—	+	Salicyl alcohol
Phenylacetic acid		—	+	Phenylacetaldehyde
Phenylacetic acid		+	—	Cyclohexanol acetate
Phenol		+	—	Cyclohexanol
Oxalic acid		—	+	Glyoxylic acid, glycolic acid

at a potential close to the null point of the corresponding metal. The existence of such effects has also been proved for the electroreduction of molecular substances and large cations.

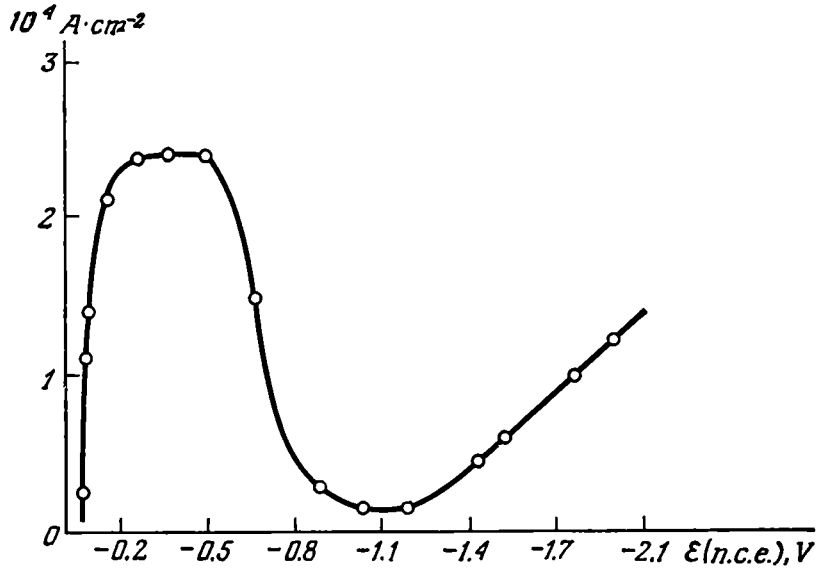


Fig. 21.1. Curve of electrochemical reduction of persulphate ion on a rotating amalgamated electrode:

$[K_2S_2O_8] = 10^{-3}$ g-eq/litre; the speed of rotation of the electrode is 3.8 revolutions per second

21.2.3. THE EFFECT OF THE SOLUTION COMPOSITION

At a given electrode potential the rate of electrolytic reduction or oxidation usually increases with increasing concentration of discharging particles. This can be seen, for example, from Fig. 21.2, which presents data on the electroreduction of trivalent manganese ions to bivalent ions. However such a simple relation is not always observed. Kinetic equations describing electrolytic reduction and oxidation reactions may contain concentrations of initial substances with exponents larger than unity, equal to zero or to a fraction. One such example was given on page 384, where the reduction of dissolved iodine to iodide was considered. In equations describing the kinetics of electroreduction of organic substances the volume concentrations of these substances are usually raised to a fractional power.

The dependence of the rate of electrochemical redox reactions on the solution pH is influenced by the nature of the reacting substances involved and also by the electrode material. At a constant potential the rate of oxygen reduction does not depend on the pH if mercury, silver or gold electrodes are used. The rate of the same reaction pro-

ceeding at Pt or Pd electrodes increases with decreasing pH of the solution. In the electroreduction of organic substances the pH of the solution may in certain cases affect not only the reaction rate but even the nature of the end products. The kinetics of redox reactions are also influenced by the presence of foreign substances of the ionic

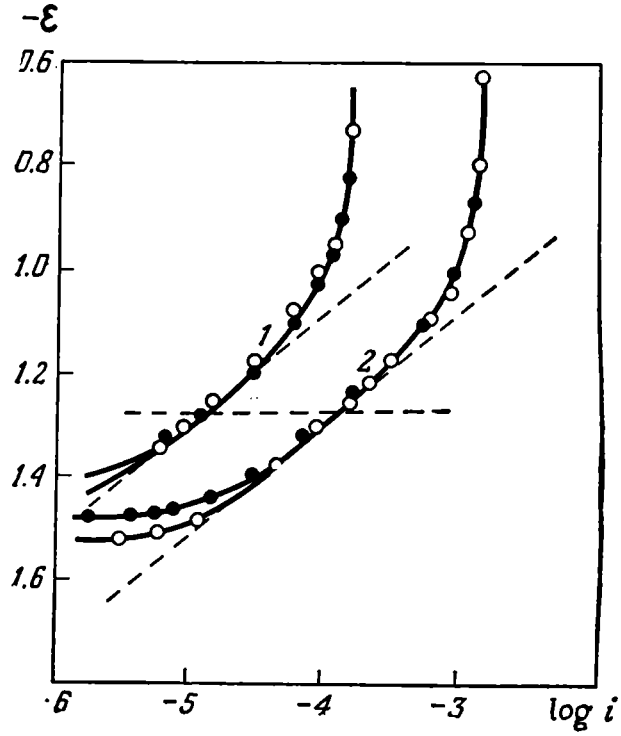


Fig. 21.2. Potential vs. current density curves for the electroreduction of Mn^{3+} ions on a platinum electrode:
1—0.001 mole/litre Mn^{3+}; *2*—0.01 mole/litre Mn^{3+}; ○—0.001 mole/litre Mn^{2+}; ●—0.01 mole/litre Mn^{2+}

or molecular type in the solution. It has been found that the reduction of anions proceeds at a faster rate in the presence of polyvalent cations. Though the dependence of the rate of redox reactions on the nature of the solvent has been studied insufficiently, the available data testify to its existence.

21.3 THE THEORY OF ELECTROCHEMICAL REDUCTION AND OXIDATION REACTIONS

In a general case the electrochemical reduction or oxidation reaction consists of the following steps:

(1) the transport of reacting particles to the electrode-electrolyte interface;

(2) the adsorption of the particles on the electrode surface (or their contact with the electrode surface) with their simultaneous or preliminary conversion to an active state;
(3) the reduction or oxidation act;
(4) the desorption of the resulting particles from the electrode surface with their simultaneous (or subsequent) transformation into the final reaction products;
(5) the removal of the reaction products from the electrode-electrolyte interface.

The most important step is the reduction or oxidation act, which determines the specificity of redox reactions.

21.3.1. POSSIBLE PATHS FOR THE ELECTROREDUCTION REACTION

The occurrence of electroreduction reactions is associated, in our opinion, with the mechanism of hydrogen evolution on a given electrode. Depending on the type of the electrode metal and the nature of the particles to be reduced the reaction rate is controlled by one of the following steps:
(1) the addition of electrons;
(2) the addition of adsorbed hydrogen atoms;
(3) the addition of hydrogen ions activated in the discharge step.

Accordingly, one may speak of three different reducing agents: electrons, hydrogen atoms and hydrogen ions.

The Rate-Determining Electron Addition Step. This step corresponds to the slow-discharge concept and is probably realizable on any electrode. The discharge act involving the addition of one or two electrons often represents the overall electrochemical reaction. Examples are the following ion-recharge processes:

$$Mn^{3+} + e = Mn^{2+}$$
$$Fe^{3+} + e = Fe^{2+}$$
$$Tl^{3+} + 2e = Tl^{+}$$
$$MnO_4^- + e = MnO_4^{2-}$$

The discharge step may also be rate determining in more complex electroreduction processes. For example, some authors believe that the reduction of quinone to hydroquinone proceeds stepwise:

$$C_6H_4O_2 + e = C_6H_4O_2^-$$
$$C_6H_4O_2^- + H^+ = C_6H_4O_2H$$
$$C_6H_4O_2H + e = C_6H_4O_2H^-$$
$$C_6H_4O_2H^- + H^+ = C_6H_4(OH)_2$$

with the addition of one electron at the first and third stages and the intermediate formation of semiquinones. According to other conceptions, this process occurs as follows

$$C_6H_4O_2 + 2e = C_6H_4O_2^{2-}$$

$$C_6H_4O_2^{2-} + 2H^+ = C_6H_4(OH)_2$$

involving the simultaneous addition of two electrons. In either case, however, the addition of one or two electrons is assumed to be the rate-determining step (rds) on the basis of kinetic relationships. If the rate of electrolytic reduction (or oxidation) is determined by the electron acception (or donation) step, its kinetics can be described by Eqs. (16.67) and (16.68):

$$i = \vec{i} - \overleftarrow{i} = zFe^{(\alpha z - z_1)F\zeta/RT}(\vec{k}c_{Ox}e^{-\alpha zF\varepsilon/RT} - \overleftarrow{k}c_R e^{(1-\alpha)zF\varepsilon/RT})$$

$$i = \vec{i} - \overleftarrow{i} = i^0 e^{(\alpha z - z_1)F\zeta/RT}(e^{\alpha zF\eta/RT} - e^{(1-\alpha)zF\eta/RT})$$

or, at a sufficient deviation from equilibrium, by Eqs. (16.65) and (16.66):

$$i_c = \vec{i} = zF\vec{k}c_{Ox}e^{(\alpha z - z_1)F\zeta/RT}e^{-\alpha zF\eta/RT}$$

$$i_a = \overleftarrow{i} = zF\overleftarrow{k}c_R e^{(\alpha z - z_1)F\zeta/RT}e^{(1-\alpha)zF\eta/RT}$$

To elucidate the nature of particles Ox directly subjected to reduction or particles R taking part in the oxidation act, the concentrations of which are included in kinetic equations, one usually utilizes data on the order of electrochemical reactions determined by Eq. (16.110):

$$\left(\frac{\partial i}{\partial c_j}\right)_{c',T,P,\varepsilon} = \nu_j$$

or by the equation

$$\left(\frac{\partial \log i}{\partial \log c_j}\right)_{c',T,P,\varepsilon} = \nu_i \qquad (21.4)$$

An interesting example of the use of these equations to identify the mechanism of redox reactions is provided by the cathodic reductions of trivalent and tetravalent manganese ions:

$$Mn^{3+} + e = Mn^{2+} \qquad (21.5)$$

and

$$Mn^{4+} + e = Mn^{3+} \qquad (21.6)$$

Some data pertaining to the first of these reactions are presented in Fig. 21.2. Curves *1* and *2* in Fig. 21.2 contain Tafel lines, for which Eq. (16.65) is valid:

$$i = zF\vec{k}c_{Ox}e^{(\alpha z - z_1)F\zeta/RT}e^{-\alpha zF\varepsilon/RT} \qquad (21.7)$$

At $\zeta = 0$ this equation may be written in the form[1)]

$$i = zF\vec{k}c_{Ox}e^{-\alpha zF\varepsilon/RT} \tag{21.8}$$

or, after taking logarithms and solving for ε,

$$\varepsilon = b \log zF\vec{k} + b \log c_{Ox} - b \log i \tag{21.9}$$

If the values of $\log i$ corresponding to two concentrations of Mn^{3+} ions, which differ by a factor of 10, are determined in the Tafel region at $\varepsilon = \text{const}$, as shown in Fig. 21.2, then one has

$$\nu_{Mn^{3+}(c)} = \left(\frac{\partial \log i}{\partial \log c_{Mn^{3+}}}\right)_{c_{Mn^{2+}},T,P,\varepsilon} \simeq \left(\frac{\Delta \log i}{\Delta \log c_{Mn^{3+}}}\right)_{c_{Mn^{2+}},T,P,\varepsilon} = 1 \tag{21.10}$$

i.e., the cathodic electrochemical order of reaction (21.5) with respect to Mn^{3+} ions is equal to unity. At the same time the change of the concentration of Mn^{2+} ions at a constant concentration of Mn^{3+} does not affect the reaction rate at a given potential, i.e.,

$$\nu_{Mn^{2+}(c)} = 0 \tag{21.11}$$

Similar calculations based on data of polarization measurements for reaction (21.6)

$$Mn^{4+} + e = Mn^{3+}$$

have shown that

$$\nu_{Mn^{4+}(c)} = \left(\frac{\partial \log i}{\partial \log c_{Mn^{4+}}}\right)_{c_{Mn^{3+}},T,P,\varepsilon} = 0 \tag{21.12}$$

At the same time the rate of reaction (21.6) increases with increasing concentration of Mn^{3+} ions. Such a result, though parodoxical at first sight, can be explained by assuming that reaction (21.6) actually consists of two steps:

$$Mn^{3+} + e = Mn^{2+}$$

$$Mn^{2+} + Mn^{4+} = Mn^{3+}$$

The reducible particles here are the Mn^{3+} ions and the acception of an electron by these ions determines the kinetics of the overall process; the subsequent disproportionation proceeds at a faster rate than the discharge of manganese ions.

The Rate-Determining Addition of Hydrogen Atoms. According to another mechanism of electroreduction its rate is controlled by the addition of hydrogen atoms to the particles to be reduced.

[1)] From Eqs. (21.8) and (21.9) it follows that when reduction occurs by the electronic mechanism the rate of the cathodic reaction and the electrode potential are independent of the solution pH.

The first step in this case is the discharge of hydrogen ions with the formation of adsorbed hydrogen atoms

$$H_3O^+ + e = H_{ads} + H_2O \qquad (21.13)$$

and the second step is the interaction of these atoms with the reducible substance:

$$H_{ads} + Ox = OxH \qquad (21.14)$$

The last step determines the rate of the overall process. For this step to occur it is necessary, first, that the discharge of hydrogen ions proceed unhindered (or with more ease than the discharge of the particles to be reduced) and, second, that the addition of a hydrogen atom to a particle Ox occur more readily than the recombination of two hydrogen atoms. These conditions are best fulfilled on metals of the platinum and iron groups and also on other metals, on which the recombination of hydrogen atoms either is the slow step or proceeds at a slow rate. The accumulation of hydrogen atoms on the surface of these metals during cathodic polarization promotes the hydration reaction. Electrochemical reduction proceeding by this mechanism is similar to the process of catalytic hydration, the only difference being that in the first case hydrogen atoms are supplied by the current and in the second by dissociation of molecular hydrogen on the catalyst surface. In accordance with the reaction equation (21.14), one can write the following expression for the reduction current density:

$$i = k_1' c_{Ox}' c_H' \qquad (21.15)$$

At a considerable coverage of the electrode surface with adsorbed hydrogen it is necessary to take into account the difference between its surface and bulk concentrations. Assuming that Freundlich's adsorption equation

$$c_H' = k_F c_H^{\beta}$$

where $0 < \beta < 1$, applies here, one can write in place of Eq. (21.15):

$$i = k_1 c_{Ox}' c_H^{\beta} \qquad (21.16)$$

Substituting the concentration of hydrogen atoms from the last equation into Nernst's formula for the hydrogen electrode gives

$$\varepsilon = \text{const} + \frac{RT}{F} \ln c_{H^+} + \frac{RT}{\beta F} \ln c_{Ox} - \frac{RT}{\beta F} \ln i \qquad (21.17)$$

The application of the thermodynamic equation of the electrode potential, which is commonly used to describe the equilibrium state, is justified here since it has been assumed that the discharge step proceeds unhindered, which is equivalent to the assumption that hydrogen ions are still in equilibrium with hydrogen atoms when

the cathodic current is flowing. From Eq. (21.17) it follows that when hydrogen atoms serve as a hydrating agent, the dependence of both the irreversible electrode potential and the potential of the reversible hydrogen electrode on the concentration of hydrogen ions obeys the same law. Metals on which electroreduction can be effected with the aid of adsorbed hydrogen atoms belong to the first electrochemical group.

The Rate-Determining Addition of Activated Hydrogen Atoms. The third possible path of electroreduction is observed when the rate of the overall process is governed by the interaction between the hydrogen ions in the double layer and the particles to be reduced:

$$H_3O^+ + Ox = OxH^+ + H_2O \qquad (21.18)$$

and when the electron addition

$$OxH^+ + e = OxH \qquad (21.19)$$

following this interaction proceeds unhindered. The mechanism of electroreduction in which the rate of the process is determined by the preliminary surface protonation of the reducible substance is most probable on mercury, lead, zinc and other metals with a high overpotential caused by the slow discharge of hydrogen ions (these metals belong to the second group). When hydrogen ions lose, during discharge, some of the water molecules forming their hydration sheath, they become more active. From the potential curves corresponding to the discharge act it follows that the higher the overpotential on a given metal the more active the hydrogen ions become before they are discharged since the deviation of the potential by the value η is equivalent to the decrease of the bond energy between the hydrogen ion and the water molecules by the product ηF. For metals of the first group this mechanism is hardly probable because hydrated ions are practically completely discharged on them owing to the considerable heat of adsorption of hydrogen and to the low activation energy of discharge. The concentration of hydrogen ions in the immediate vicinity of the electrode surface may considerably exceed their concentration in the bulk of the solution.

The discharge of hydrogen ions with the formation of adsorbed hydrogen atoms

$$H_3O^+ + M + e = M{-}H + H_2O \qquad (21.20)$$

in the presence of reducible particles may also follow a two-step path and involve the formation of end products through addition of hydrogen to these particles. This electroreduction process will prevail if it is kinetically more advantageous, for example, if the energy level of the system OxH is lower than that of the system

MH (Fig. 21.3). The reducible particle will here play the role of a "bridge" facilitating the transfer of an electron from the electrode to the hydrogen ion. If step (21.18) is rate limiting, then, using

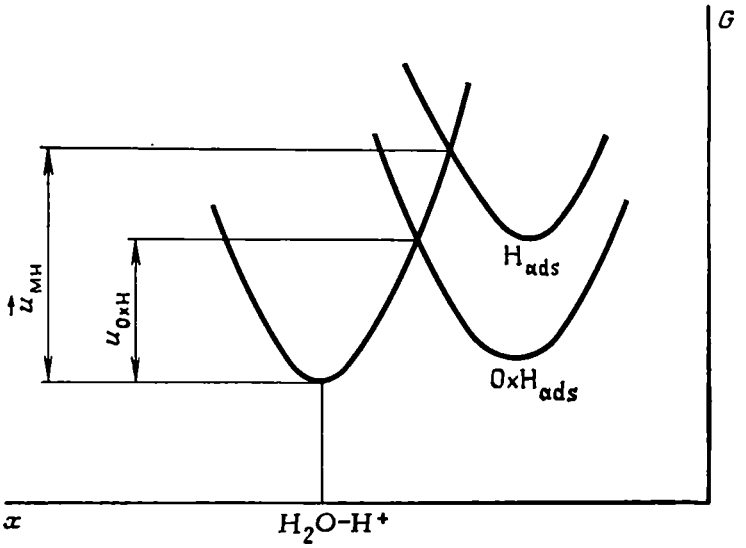


Fig. 21.3. Discharge of hydrogen ions in the presence of a reducible organic substance

the slow-discharge theory, one can write the following expression for the rate of surface protonation:

$$i = k_1 c'_{Ox} c'_{H+} e^{-\alpha F\varepsilon/RT} \qquad (21.21)$$

Assuming the surface concentration of hydrogen ions to be proportional to their bulk concentration, one gets

$$\varepsilon = \text{const} + \frac{RT}{\alpha F} \ln c_{H+} + \frac{RT}{\alpha F} \ln c'_{Ox} - \frac{RT}{\alpha F} \ln i_c \qquad (21.22)$$

In this case the electrode potential must vary with the hydrogen-ion concentration according to a law different from the one which was valid for the equilibrium hydrogen electrode.

The concept of surface protonation as a step determining, under certain conditions, the rate of electroreduction, the probability of the occurrence of this step for different cathodes and also general equations describing its rate were discussed earlier (Antropov, 1950-54). Later these conceptions were substantially developed by other researchers, particularly by Mairanovsky, who considered a probable protonation mechanism for the special case of mercury cathodes. He made a distinction between surface and bulk protonation, took into account the possibility of the change of the protonation rate due to the difference between the hydrogen-ion concentra-

tions in the bulk of the solution and at the electrode surface and also derived some additional kinetic equations.

The conception of the possibility of electroreduction proceeding by different paths with the rds involving different reducing agents (the choice of which is dictated by the nature of the slow step of hydrogen evolution on a given metal) permits interpretation of a large number of experimental data. In particular, this concept enables one to account for the existence of selective reduction (see Table 21.1). The reduction of organic substances at platinum and nickel cathodes is evidently accomplished at the expense of adsorbed hydrogen atoms which add on to nonpolar bonds (of the double or triple type) between carbon atoms. Reduction at mercury and lead cathodes proceeds at the expense of hydrogen ions which add on more readily to negative polar groups (e.g., carbonyl or carboxyl groups).

The different occurrence of electroreduction on platinum and mercury has been confirmed by a comparison of experimental results with the theoretical equations (21.9), (21.17) and (21.22). For example, the electroreduction of nitrobenzene and acetone on mercury proceeds through a surface protonation step. On platinum, nitrobenzene is reduced in the presence of adsorbed hydrogen atoms, while acetone is not reduced at all.

Analogous results have been obtained in studies of the electroreduction of oxygen. This reaction plays the crucial role in processes of metal corrosion and in the operation of cells with air depolarization. It has received much attention in recent years in connection with the problem of direct conversion of chemical energy into electrical power by means of fuel cells. The basic kinetic regularities of oxygen reduction in acidic and alkaline mediums have already been established (Tomashov, Krasilshchikov, Iofa, Bagotsky, and others). For example, it has been found that the electroreduction of oxygen on mercury, silver, and gold can be described by the following equations

$$\varepsilon = \text{const} + b \log c_{O_2} - b \log i \qquad (21.23)$$

for acidic solutions and

$$\varepsilon = \text{const} + b \log c_{O_2} - b \log c_{OH^-} - b \log i \qquad (21.24)$$

for alkaline solutions. Equation (21.23) coincides with Eq. (21.9) derived for the slow addition of one electron to a reacting particle—in this particular case, to an oxygen molecule

$$O_2 + e = O_2^-$$

Equation (21.24) also corresponds to the slow addition of an electron, this time not to an oxygen molecule but to the radical HO_2 formed in the reduction reaction. The end product of the reaction is hydrogen

peroxide:

$$HO_2 + e = HO_2^-$$
$$HO_2^- + H^+ = H_2O_2$$

When platinum or palladium electrodes are used, the kinetics of electroreduction is essentially different. Here, experimental data agree with the equation

$$\varepsilon = \text{const} + b^0 \log c_{H^+} + b^0 \log c_{O_2} - b^0 \log i \qquad (21.25)$$

which at $\beta = 1$ coincides with Eq. (21.17) derived under the assumption that the interaction of adsorbed hydrogen atoms with reducible particles proceeds at a slow rate. In the case of Pt or Pd electrodes adsorbed hydrogen atoms interact with oxygen molecules:

$$H_3O^+ + e = H_{ads} + H_2O$$
$$H_{ads} + O_2 = HO_2$$

Then the radical HO_2 undergoes transformations leading to the formation of hydrogen peroxide. To bring Eq. (21.17) into agreement with the experimentally found relation (21.25) one must assume that $\beta = 1$. This assumption may be regarded as physically quite justifiable. The equality $\beta = 1$ corresponds to the direct proportionality between the bulk and surface hydrogen concentrations, which is realizable at a low coverage of the electrode surface with adsorbed particles. The cathodic reduction of oxygen corresponds to this condition because the electrode potential here is shifted to the positive side from the potential of the reversible hydrogen electrode to such an extent that the surface concentration of hydrogen atoms must be very low.

The electroreduction of oxygen proceeds without rupture of the bonds in the initial molecule and involves the formation of hydrogen peroxide as an intermediate. Conditions can be realized, however, under which the electrochemical reduction of oxygen will follow a different path—via the decomposition of its molecule into atoms without formation of hydrogen peroxide:

$$O_2 = 2O_{ads}$$
$$2O_{ads} + 4H^+ + 4e = 2H_2O$$

The electrolytic oxidation of organic substances has been studied to a considerably lesser degree than the reactions of cathodic reduction. It was not until recently that this field of electrochemical kinetics had come into focus in connection with the utilization of organic substances in fuel cells. The data available at present indicate that, as in electroreduction, the electrode material plays an important role in this case, too. For example, the electrolytic

oxidation of a number of organic substances, in particular lower alcohols, on metals of the first electrochemical group (platinum, nickel) proceeds by the dissociative mechanism with the splitting-off of hydrogen (dehydrogenation) and radical formation:

$$RH_m = RH_{(m-k)ads} + kH_{ads}$$

Both the radical and the adsorbed hydrogen can be subjected to further transformations. Conversely, on metals of the second group the oxidation of the same substances does not proceed through the preliminary dehydrogenation step.

Other Paths for Electrolytic Reduction and Oxidation. The three versions discussed above do not cover all possible paths for redox reactions. The role of reducing and oxidizing agents can also be played by metallic ions present in solution. In this case the electrode process reduces to the oxidation (or reduction) of metallic ions variable valency, which then reduce (or oxidize) the organic substance. The electrolytic oxidation of an anthracene suspension may be quoted as an example. When this suspension is subjected to electrolysis, the anodic current is almost completely consumed for oxygen evolution. If, however, a small amount of a cerium, chromium or manganese salt is added to the suspension, then, apart from oxygen, anthraquinone is also formed on the anode. The reaction evidently proceeds as follows: the ions of a metal, say, cerium, are oxidized at the anode:

$$Ce^{3+} = Ce^{4+} + e$$

and then react with anthracene, which is thus converted into anthraquinone:

$$6Ce^{4+} + C_{14}H_{10} + 2H_2O = 6Ce^{3+} + C_{14}H_8O_2 + 6H^+$$

The cerous ions formed are again oxidized to ceric ions according to the first equation. Thus, here only the intermediate reaction—the recovery of tetravalent ceric ions—occurs as an electrochemical process on the electrode surface, while the oxidation of anthracene takes place in the bulk of the solution and is a purely chemical reaction independent of the electrode potential. The transfer of the reaction from the electrode surface into the bulk of the solution can be effected not only by introducing special substances but by the reactants themselves—free radicals, and other active particles capable of initiating a chain reaction. The oxidation reaction may involve the formation of intermediates, which serve as an autocatalyst (Khomutov).

The concept of the electrochemical reduction and oxidation reactions will be substantially changed if one assumes the participation of solvated electrons $\bar{e}_s$ in these reactions. In this case the

primary act of reduction is the formation of solvated electrons near the cathode

$$\bar{e}_{[M]} + L = \bar{e}_s$$

and the primary act of oxidation, the splitting-off of an electron from the oxidized particle and its solvation:

$$R + L = R^+ + \bar{e}_s$$

The secondary reduction act is the addition of the solvated electrons to the particles to be reduced:

$$Ox + \bar{e}_s = Ox^- + L$$

and the secondary oxidation act is the transfer of the solvated electrons to the anode:

$$\bar{e}_s = \bar{e}_{[M]}$$

Further transformation of particles R^+ and Ox^- depends on their nature and on the conditions of the corresponding reactions.

When solvated electrons are involved, redox reactions are no longer purely heterogeneous processes taking place at the electrode-electrolyte interface; they now occur at a certain distance from it, in the bulk of the solution.

The probability of such reactions taking place in the solution and the distance from the electrode surface must be the greatest in solvents, in which the lifetime of solvated electrons is maximal. Such processes are of great interest to theoretical electrochemistry.

21.3.2. THE ROLE OF ADSORPTION PHENOMENA IN ELECTROCHEMICAL REDOX REACTIONS

The adsorption of reacting particles on the electrode surface is not a necessary precondition for electrochemical redox reactions. However, it usually plays an important role, and neglect of this phenomenon leaves a gap in the theory of redox reactions.

It is thought that even in the case of simple redox reactions (ion recharge), adsorption phenomena influence the kinetics of electrode processes. Indeed, during electroreduction ions of higher valency M^h (we will call them primary ions) are converted into ions of lower valency M^n (secondary ions), which are not subjected to further reduction under the electrolysis conditions chosen. Ions M^n are formed at the same site where ions M^h resided previously. If the removal of the M^n ions from the electrode surface is hampered, the reduction will be slowed down since the approach of reducible particles to the surface is made difficult and their concentration on the electrode surface decreases. In order to quit the electrode surface secondary ions have to overcome a certain barrier associated

with the difference in their energy levels in the bulk of the solution and at the interface. But since primary ions can occupy their site, the actual energy barrier will depend on the probability of an energy exchange and gain during adsorption of primary ions, i.e., in the long run on the potential and charge of the electrode and also on the concentration and nature of the ions. If the positive charge of primary (reducible) ions is higher than that of secondary ions, the shift of the potential to the negative side must be more favourable for adsorption of primary ions, which facilitates the removal of the reaction products. These conditions are realizable, for example, when iron ions Fe^{3+} and Fe^{2+} and thallium ions Tl^{3+}, Tl^{+} are recharged, because the difficulties associated with the desorption of Fe^{2+} or Tl^{+} ions are not great in electroreduction. Conversely, if in electroreduction the positive charge of primary ions is lower than that of secondary ions, then the difficulties due to the necessity of desorption of the latter must be considerable. This is observed, for example, in the reduction of CeO^{2+} ions to Ce^{3+}. The greatest hindrances should be expected in those cases where primary ions are charged negatively and secondary ions positively (the reduction of a metavanadate ion VO_3^- to a vanadyl ion VO^{2+}). These assumptions are in agreement with the experimental data obtained in the recharge of iron, cerium, thallium, vanadium and molybdenum ions.

Adsorption phenomena assume still greater importance in the case of electrolytic reduction and oxidation of organic substances. Neglect of adsorption would make it impossible to account for the frequently observed seemingly fractional order of the electroreduction reaction. It is known that the fractional order is characteristic of heterogeneous catalytic processes involving adsorbed particles. The fractional reaction order reflects the difference between the bulk and surface concentrations of these particles. It is interesting to note in this connection that the exponent of the bulk concentration of acetone is found to be the same both in the kinetic equation describing the process of its electroreduction on a mercury cathode and in Freundlich's equation describing the adsorption of acetone on mercury. This result, coupled with the data obtained in studies of the effect of pH on the kinetics of the process, has led to the conclusion that the electroreduction of acetone on mercury in acidic solutions is a first-order reaction with respect to both acetone and hydrogen ions.

The occurrence of an electroreduction reaction via the adsorption step is more probable and energetically more advantageous even in those cases when the surface coverage with depolarizer particles is very low.

The degree of adsorption on the surface of an electrode depends on its potential or, more exactly, on its charge, a circumstance

that must leave its imprint on the kinetics of electroreduction processes if they involve adsorbed particles. To find out the role of a surface charge in electroreduction it should be recalled how the shape of electrocapillary curves is affected by surface-active substances. The highest adsorbability of organic molecular substances is observed near the null point of mercury (see Fig. 10.2, page 250). When the deviation from this point is considerable, organic substances are displaced from the metal surface and cease to affect the shape of the electrocapillary curve. Suppose that the potential at which a given substance is capable of undergoing reduction corresponds to a certain value ε_R marked by a vertical line in Fig. 10.2*c*. At this potential value the surface concentration of the organic substance is sufficiently high, which is evidenced by the value of the surface-tension decrement $\Delta\sigma$. An increase in the cathodic potential, i.e., a rise in the overpotential, reduces $\Delta\sigma$ due to the drop in the surface concentration of the organic substance which creates it. This will accordingly decrease the rate of electroreduction. At still higher negative values of the potential, when the surface-tension decrement $\Delta\sigma$ is equal to zero, the surface concentration of the organic substance becomes so small that no depolarizer molecules are found on the electrode surface, and in their absence electroreduction is naturally impossible. Thus, not only the values of the cathodic potential and the hydrogen overpotential (the deviation of the potential from the equilibrium value) are important for the process of electroreduction but also the potential on the correlative scale, which characterizes the magnitude and sign of the charge on the metal surface.

Suppose that the electroreduction of a substance on different metals is carried out at one and the same value of the cathodic potential, say, at —0.8V on the hydrogen scale. Mercury, lead, zinc and silver are used as the cathode. All these metals belong to the first electrochemical group and hence do not differ in the nature of the reducing agent. But even in this case the reaction conditions on these metals will be different at the same cathodic potential. This is attributed to the difference in their charges and in the degree of adsorption of the reducible substance. The null points (see Table 10.5, page 278) of these metals are as follows: —0.2V for mercury, —0.7V for lead, —0.5V for zinc, and —0.4V for silver. At the same cathodic potential (—0.8V) the potentials of these electrodes on the correlative (reduced) scale will therefore be different. They will be equal to —0.8— (—0.2) = —0.6V for mercury, —0.8— (—0.7) = —0.1V for lead, —0.8 — (—0.5) = —0.3V for zinc, and —0.8 — (—0.4) = = —0.4V for silver. As follows from Fig. 21.4, at these values of the φ potential the most favourable conditions for electroreduction are attained when zinc and, especially lead cathodes are used; these conditions are much less favourable on mercury. The magnitude

of the surface-tension decrement $\Delta\sigma$ falls precisely in this order, and so does the surface concentration of the reducible substance. As to platinum, the conditions on it are still less favourable for electroreduction since at the potential chosen (—0.8V) its φ potential, which is equal to $-0.8 - (+0.2) = -1.0$V, lies beyond the limits of perceptible adsorption of an organic substance[1]. In the

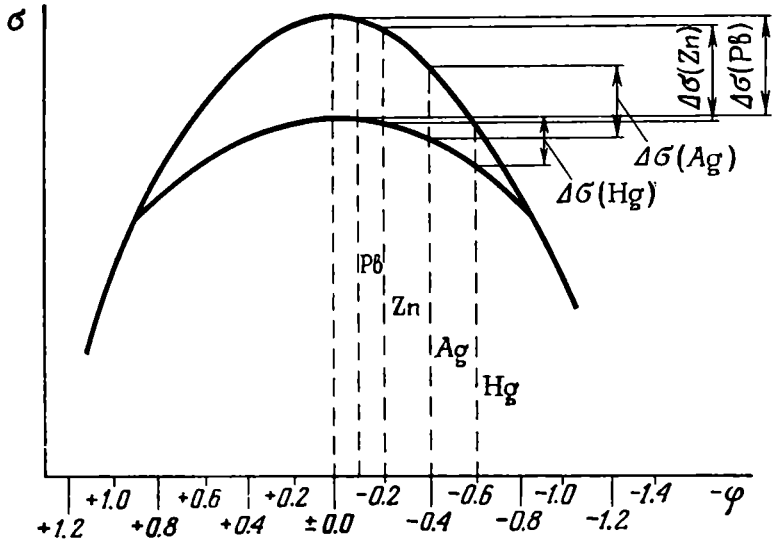


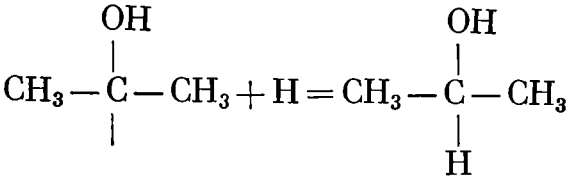
Fig. 21.4. The effect of the charge of the electrode surface on the adsorption of organic substances in their electroreduction at a cathodic potential of $\varepsilon = -0.8$V; σ is the surface tension and φ the potential on the correlative scale

electroreduction of acetone in an acid medium the highest current efficiency is observed on lead and zinc cathodes; it is much less on mercury and is equal to zero on platinum. The magnitude of the surface charge exerts an influence not only on the efficiency of an electroreduction reaction; in many cases it also determines the nature of the end products. For example, the electroreduction of acetone may yield two principal end products: isopropyl alcohol and pinacol. Considering that this is a first-order reaction with respect to acetone, the first step can be represented as follows:

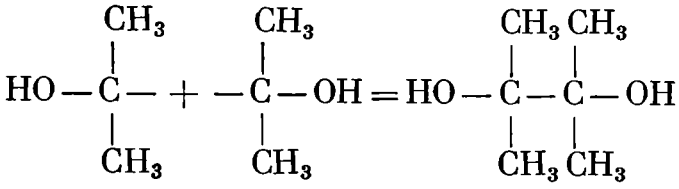
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H = CH_3-\overset{\overset{OH}{|}}{\underset{|}{C}}-CH_3$$

[1] At one and the same electrode potential the electroreduction conditions on platinum will be different also because of the different nature of the reducing agent.

The free radicals formed can be either reduced to yield isopropyl alcohol:



or recombined to produce pinacol:



Since the rate of the formation of isopropyl alcohol depends on the surface concentration of radicals to the first power and that of pinacol, to the second, a measurable yield of pinacol can be obtained only when the surface concentration of free radicals is sufficiently high under given electroreduction conditions. This requirement must be best fulfilled for lead cathodes, on which the current yield of pinacol is the highest in fact.

On the basis of the foregoing one can draw the following conclusions.

1. The course of electrochemical redox reactions depends not only on the cathodic potential (the overpotential) but also on the charge of the metal surface, which is determined, to a first approximation, by the value of the φ potential (the deviation of the electrode potential under given conditions from the null point of the electrode metal). Here the overpotential serves as a measure of the reducing or oxidizing action of the electrode under given conditions, and the φ potential determines the surface concentration of depolarizer.

2. The equality of the potentials of different electrodes does not yet provide identical conditions for a redox reaction since the null points of metals are different. Depending on the null point of the electrode metal used, the same value of the potential may correspond to different surface charges and hence to different conditions of depolarizer adsorption.

3. The values of the ε and φ potentials combined determine not only the effectiveness but also the direction of the electrochemical redox reaction and also the most probable nature of its end products. The closeness of the reduction (or oxidation) potential to the null point of the electrode usually promotes the formation of bimolecular reaction products.

4. An increase in the cathodic potential changes the surface charge and hence the conditions of adsoption on the cathode. Depending on the nature of the depolarizer chosen, this either accelerates or retards the electrochemical redox reaction. At considerable deviations from the null point (which implies a high value of the φ potential) the surface concentration of the depolarizer becomes negligibly small and the electroreduction may stop. Therefore, apart from the diffusion limiting current density, there must also exist an adsorption limiting current density.

These considerations expressed by Antropov in 1954 are associated neither with the assumption as to nature of the slow step nor with any special assumption concerning the nature of the forces responsible for the change of the depolarizer adsorbability with potential. They are based only on the results of purely experimental studies of electrocapillary phenomena and also on the concept of the correlative potential scale.

The effect of the charge of the electrode on adsorption and hence on the kinetics of electroreduction can also be expressed quantitatively, using the concept of the correlative scale and introducing the φ-potential function into the kinetic equation:

$$i = k_1 c_{Ox} e^{-\alpha z F \varepsilon / RT} e^{f(\varphi)} \qquad (21.26)$$

The form of the function $f(\varphi)$ is governed by the law of variation of the surface concentration of reducible particles with deviation of the potential from the null point. For organic molecular substances, the approximate expressions of this law are Frumkin's and Butler's equations [Eqs. (10.39) and (10.40), respectively]. It is these equations that were used by Antropov in 1945-50 in writing Eq. (21.26) in expanded form. Equation (21.26) is of considerable interest since it is the first kinetic formula which, apart from the electrode potential on the conventional hydrogen scale, contains also the electrode potential on the correlative scale, which is a function of the null point of a metal. Later, Kheifets (1949) and Bockris and Potter (1952) proposed independently somewhat different formulas reflecting the role of the null point in the kinetics of electrode processes. Recently this problem once again attracted the attention of electrochemists (Mairanovsky, Teodoradze, Moliner, Delahay, and others) and was elaborated further.

The effect of the charge on adsorption must reveal itself not only when organic molecular substances participate in electrochemical reactions. The desorption of anions occurs at still smaller deviations to the negative side from the null point of a metal than the desorption of unionized particles (see Fig. 10.2, page 250). This suggests that when anions are discharged, the decrease in the rate of electroreduction must be more pronounced and can be effected more easily than in the electroreduction of organic molecules.

This decay of the current was detected by Kryukova (1949) in the electroreduction of persulphate ions. Kryukova ascribed this effect to the change of the surface concentration of persulphate ions under the influence of the electric field in the double layer. This current decay may be regarded as the first experimental proof of theoretical predictions made by Antropov on the basis of electrocapillary measurements. It should be stressed at the same time that the phenomenon observed by Kryukova and known as the Kryukova effect is not restricted to the current fall. After the current drops to a certain minimum value, it mounts up again (see Fig. 21.1), i.e., the process of electroreduction is resumed. The latter point does not follow directly from electrocapillary data.

The Kryukova effect theory suggested by Frumkin is based on the assumption that the rate of the electroreduction of an anion is determined by the discharge step. If the reverse reaction is ignored, one can write the following equation for the discharge current density:

$$i = k_1' c_{Ox}' \exp\left\{-\frac{\alpha(\varepsilon-\zeta)F}{RT}\right\} \qquad (21.27)$$

where c_{Ox}' is the surface concentration of anions and $(\varepsilon - \zeta)$ is the potential drop in the Helmholtz region of the double layer. Using the Stern equation to relate the bulk (c_{Ox}) and surface (c_{Ox}') concentrations of anions and substituting the value of the latter into Eq. (21.27), one obtains

$$i = k_1 c_{Ox} \exp\left\{\frac{(\alpha+z)F\zeta}{RT} - \frac{\alpha F\varepsilon}{RT}\right\} \qquad (21.28)$$

where z is the valency of the anion. Equation (21.28) contains two potential-variant factors. One of them, $\exp\{-\alpha F\varepsilon/RT\}$, increases continuously as the value of ε is shifted to the negative side and the other, $\exp\{(\alpha+z)F\zeta/RT\}$, falls with decreasing degree of diffusion in the double layer. The greatest change of the ζ potential is observed near the null point and therefore its effect is found to be predominant here, which results in a current fall. With further increase of the cathodic polarization the ζ potential changes more gradually and the second factor becomes decisive, which results in a current rise. Frumkin's theory thus accounts for the current fall and rise on the polarization curve. This theory is also in accord with experimental findings concerning the effect of extraneous (indifferent) ions on the electroreduction of anions. Frumkin's theory however fails to explain the changes in the shape of reduction polarization curves observed when going from one type of reducible anions to another.

We have so far considered the role of adsorption only in the electrolytic reduction (or oxidation) reaction proper. Adsorption must also affect the kinetics of competing reactions, i.e., the kinetics

of hydrogen or oxygen evolution. The presence of adsorbed substances on the electrode surface may either increase or decrease the hydrogen or oxygen overpotential. This in turn will alter the conditions of reduction or oxidation reactions. These conceptions are in conformity with the experimental fact that the electrochemical reduction or oxidation of many substances often proceeds with a considerable current efficiency at potentials markedly higher than those at which (for the same current density) hydrogen or oxygen is evolved from solutions containing no depolarizer. For example, the Kolbe synthesis is feasible just because organic substances adsorbed on a platinum electrode poison it, thereby hindering oxygen evolution and shifting the potential to a value at which anions of carbonic acids can begin to oxidize (Antropov, 1946). At first glance the adsorption of organic substances at such positive potentials seems to be impossible. It is necessary however to take into account that the oxidation of the electrode surface results in an increase in the electronic work function and hence in a shift of the uncharged-surface potential to the positive side. In isolated cases the value of ζ changes by one volt or more. Therefore, when the potential of a given metal is shifted from the most negative to the most positive values, it may happen that not one but two or more maxima of the adsorption of organic substances appear near the corresponding uncharged-surface potentials.

CHAPTER 22
Electrodeposition of Metals from Solutions

22.1. GENERAL DESCRIPTION OF THE PROCESS

The electrochemical deposition of metals from aqueous solutions of their compounds lies at the basis of hydro- and electrometallurgical processes, i.e., extraction of metals from their ores (*electrowinning*) and their purification (*electrorefining*) by electrolysis. Among the metals produced and refined by hydro- and electrometallurgical processes are copper, nickel, zinc, cadmium, tin, lead, silver, gold, manganese, etc. Technically pure metals can be produced and metals recovered profitably from low-grade ores by hydro- and electrometallurgy. The electrochemical deposition of metals is used to protect the basis metal from corrosion by coating it with more stable metals or alloys and also to impart a pleasing, decorative appearance to articles (electroplating). Another use of metal electrodeposition is for producing replicas and reproducing works of art, for the manufacture of strips, seamless tubes, printed circuits, etc. (*electroforming* and *electrotyping*). The possibility of using electrolysis with metal deposition to satisfy practical demands was first indicated in 1837-38 by the Russian Academician Yakobi, who can be rightly called the inventor and founder of electroplating and related processes.

Metals are generally electrolytically deposited from solutions of their simple salts—sulphates, chlorides or nitrates. The overall cathodic reaction in this case is the discharge of hydrated metallic ions with their subsequent incorporation into the crystal lattice of a cathodically formed deposit:

$$M^{z+} \cdot xH_2O + ze = [M] + xH_2O \qquad (22.1)$$

The cathodic deposition of metals from solutions of their complex ions with a net positive (or negative) charge also finds wide use, especially in electroplating. For solutions containing complex ions the overall reaction of cathodic metal deposition may be written as follows:

$$MA_x^{z-x} + ze = [M] + xA^- \qquad (22.2)$$

where z is the valency of the metal in the complex MA_x^{z-x}.

The electrochemical deposition of metals from aqueous solutions always occurs at a more electronegative potential than the equili-

brium potential of the corresponding metal under given conditions. The difference in potential between an electrode at equilibrium and an electrode subjected to an external current (i.e., in the cathodic deposition of metals) corresponds to the electrode polarization

$$\Delta\varepsilon = {}_{M}\varepsilon_i - {}_{M}\varepsilon_r \qquad (22.3)$$

That part of the total polarization which is not associated with the slow transport process is often called the metal overpotential. The magnitude of overpotential is here also related to the nature of the electrode process.

As in other electrode reactions, in the electrochemical deposition of metals the polarization is dependent on current density, increasing with it. In this case, however, the form of this dependence is often

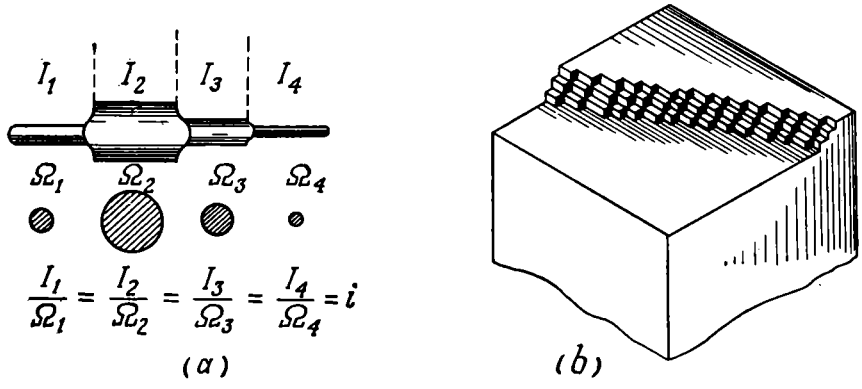


Fig. 22.1. Various growths of a cathodic deposit:

a—variation of the cross-section of a needle-like crystal with current density ($I_1/\Omega_1 = I_2/\Omega_2 = I_3/\Omega_3 = I_4/\Omega_4 = i$; *b*—spreading of a deposit over the cathode surface in the form of a thick packet

more complicated. Even for the deposition of the same metal, the results of polarization measurements may take the form (depending on the range of current densities used, solution composition and temperature) of straight lines in one of the following coordinate systems:

$$\eta - i,\ \eta - \log i,\ \frac{1}{\eta} - \log i,\ \frac{1}{\eta^2} - \log i$$

Experimental investigation of the kinetics of the cathodic deposition of metals is a complicated task, because of the specific features of this process. The cathode surface does not remain intact during electrolysis, it changes all the time as the metal is being deposited. The growth of a deposit is essentially dependent on the nature of the metal and electrolysis conditions. Some metals, e.g. silver and thallium, are characterized by the formation of very thin needle-like crystals called whiskers and dendrites. By watching the growth of a needle-like crystal one can see that its cross-section is changed as the applied current is varied. Often (see Fig. 22.1*a*) the needle-

like crystal becomes thicker with increasing current and, conversely, its thickness diminishes as the current falls (Samartsev, Gorbunova, Vagramyan). The surface, on which metal deposition occurs, adapts itself, as it were, to the current in such a manner that the current density and, hence, the linear rate of growth of the crystal remains approximately the same. Not infrequently lamellar growth of a deposit is observed, in which case the crystalline packet moves at a definite rate along the cathode surface (Fig. 22.1*b*). The metal is

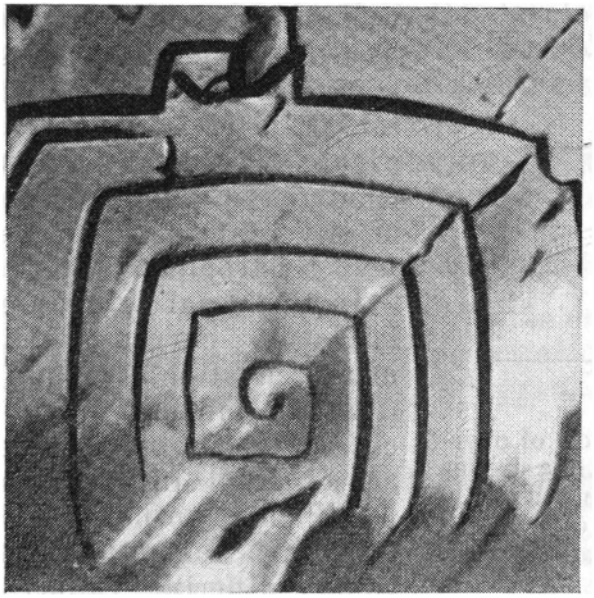


Fig. 22.2. Micrograph of the spiral growth of a silver deposit (after Kaischew)

deposited not on the entire surface but only on the slope of the packet, which is thus the actual advancing crystal front. By studying the conditions under which a deposit is formed on a single crystal of silver it was found that the crystal grows regularly along one or several spirals. Figure 22.2 shows a typical micropicture of the spiral growth of silver.

The specificity of the growth of electrolytic metal deposits makes it difficult to measure the current density or, in other words, the rate of an electrochemical process. Here one should distinguish between the apparent current density, i.e., the current per unit of geometrical (visible) surface area of the electrode, and the true current density, which is equal to the ratio of the current to the active surface area, i.e., to the actual growth surface of the deposit. During the formation of a cathodic deposit the true current density may vary with the apparent current density remaining constant.

Study of the kinetics of electrodeposition of metals is also associated with difficulties due to the time variation of the cathode potential. The variation of the potential and of electrode polarization is caused not only by the change of the active surface area and of true current density but by other factors as well. The time variation of the potential is especially pronounced during the deposition of metals on electrodes of other metals when electrolysis gives rise to a new metallic phase, for example, during the deposition of cadmium, copper, silver, mercury, and a number of other metals on a platinum cathode. This phenomenon was first detected by LeBlanc in 1910. The overpotential is found to vary with time also during the deposition of a metal at a cathode of the same metal. Figure 22.3 is a typical polarization-time curve obtained in the deposition of silver at a silver cathode (Samartsev, Evstropiev).

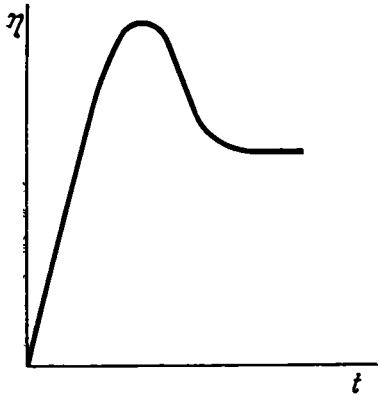


Fig. 22.3. Variation of overpotential with time frequently observed in the cathodic deposition of a metal (after Samartsev and Evstropyev)

In the usual procedure of tracing polarization curves the potentials are measured after a certain lapse of time from the moment when a new value of current is applied. These time intervals are different in experiments carried out by different authors. As follows from the time variation of the potential (Fig. 22.3), widely differing values of polarization are obtained at the same current density, which makes the data of different authors incomparable.

The nature of a deposit and the conditions of its formation in time at a constant current (or at a constant potential) depend not only on the type of the metal but also, to a large degree, on the solution composition and the impurities present in solution. The presence of surface-active substances and also of various oxidizing substances (e.g. dissolved oxygen) affects the kinetics of metal electrodeposition. The degree of purity of the solution and the nature of the impurities may affect the crystal growth, the number of crystallization centres arising in unit time on a unit surface area of the cathode, the polarization at a given current density, its variation with time, etc.

In those cases where the cathodic yield of a metal is lower than unity (electronegative metals, high current densities) complications arise, which are associated with the variation (usually, the increase) of the pH in the catholyte owing to hydrogen evolution. The alkalization of the solution near the cathode favours the hydrolysis of the metal's salts with the formation of its basic salts and hydroxides,

which can affect the course of electrodeposition and be incorporated into the cathodic deposit.

In spite of serious difficulties encountered in experiments and in theoretical interpretation of the results obtained due to the specific features of metal deposition processes, a large body of factual material has been accumulated and definite conceptions have emerged concerning the nature of these processes. Sufficiently reliable data can now be obtained owing to the improved experimental technique (new methods of investigation, which make it possible to avoid complications associated with the peculiarities of crystal lattice buildup and time variation of potential); the development of procedures for measuring the growth surface and, accordingly, the true current density; thorough purification of solutions, etc.

22.2. THE EFFECT OF VARIOUS FACTORS ON CATHODIC DEPOSITION OF METALS

22.2.1. THE ROLE OF THE METAL NATURE

In the electrolysis of solutions of simple salts the nature of cathodic deposits and the magnitude of electrode polarization are primarily determined by the type of the metal being deposited (Table 22.1).

TABLE 22.1

Classification of Metals According to Overpotential in Deposition from Solutions of Their Simple Salts

Property	Metal		
	Hg, Ag, Tl, Pb, Cd, Sn	Bi, Cu, Zn	Co, Fe, Ni
Overpotential, V	0 to $n\times10^{-3}$	$n\times10^{-2}$	$n\times10^{-1}$
Exchange current, A/cm^2	$n\times10^{-1}$ to $n\times10^{-3}$	$n\times10^{-4}$ to $n\times10^{-5}$	$n\times10^{-8}$ to $n\times10^{-9}$
Mean linear dimensions of grains, cm	$\geqslant10^{-3}$	10^{-3} to 10^{-4}	$\leqslant10^{-5}$

All the metals listed in Table 22.1 are divided into three groups. One group includes metals deposited from aqueous solutions either without overpotential (mercury) or at an overpotential not exceeding several millivolts at ordinary current densities (silver, thallium, lead, cadmium, and tin). The time variation of potential, the intricate growth of the cathodic deposit and other characteristic features of the cathodic deposition of metals are manifested most distinctly for this group of metals (except mercury). At industrial current densities these metals form rough deposits with coarse grains reaching several tens of microns across. Exchange currents are very high

for metals of this group. For example, the exchange current between metallic mercury and a solution of mercury nitrate reaches 4×1^{-1} A/cm^2, that between silver and a solution of silver nitrate reaches 1×10^{-2} A/cm^2, and that between cadmium and a solution of cadmium sulphate, 10^{-3} A/cm^2.

Bismuth, copper and zinc form the intermediate group. In the case of these metals the overpotential is of the order of several tens of millivolts, thinner deposits are formed (the mean grain size does not exceed 10 μ) and the exchange currents are smaller than those for the metals of the first group. For example, the exchange current between copper and a solution of copper sulphate is close to 10^{-5} A/cm^2.

The highest metal overpotential is exhibited by metals of the iron group where it reaches several tenths of a volt. These metals are deposited on the cathode in the form of dense fine-grained formations. Exchange currents are small: 10^{-8} and 10^{-9} A/cm^2 for iron and nickel, respectively, in solutions of their sulphates.

The data presented in Table 22.1 refer to ordinary electrolysis conditions under which a metal is deposited on a polycrystalline substrate and forms deposits having also a polycrystalline structure. The surface of such deposits is formed by faces of different crystallographic indices. Which faces will predominate on the deposit surface depends on the conditions of electrodeposition. It is therefore important to find out whether the metal overpotential depends on which face the metal is deposited on. The existence of this dependence has been confirmed by experiments with single crystals of a number of metals with different faces oriented towards the solution. From Table 22.2 (after Piontelli) it follows that in the

TABLE 22.2

Dependence of Metal Overpotential (mV) on Single Crystal Face Index at $i = 10$ mA/cm^2 and $t = 25$°C

Face index	Metal and solution			
	Pb	Sn	Cu	Ni
	0.5*M* $Pb(ClO_4)_2$, 0.5*M* $HClO_4$	0.5*M* $SnCl_2$, 0.5*M* HCl	0.5*M* $Cu(ClO_4)_2$, 0.5*M* $HClO_4$	10*M* $NiCl_2$, 0.33*M* H_3BO_3, pH = 3.1
(100)	3.0	2.5	35	786
(110)	3.0	4.0	30	809
(111)	4.4	—	43	819

case of metals of low overpotential a change from one face to another causes a considerable relative change of overpotential. For example,

a change from the (111) face to (110) during the deposition of lead decreases the overpotential from 4.4 to 3.0 mV, i.e., almost by one and a half times. For copper, the relative effect of the face index is less pronounced, and the maximum difference in overpotential does not exceed 40 per cent, though the absolute variation of overpotential in changing from one face to another is here much wider than in the previous case. When nickel was deposited, the maximum difference in overpotential was observed for the (111) and (100) faces, where it reaches 80 mV. The nature of the face is not so essential in this case since the relative variation of overpotential is only 3 to 4 per cent. From Table 22.2 it also follows that the maximum value of metal overpotential depends on the type of metal rather than on the crystallographic orientation of the electrode surface. No matter on which face the metal is deposited, the overpotential is always higher for nickel than for copper, and for copper than for tin and lead.

The secondary role of crystallization factors in overpotential phenomena is also evidenced by data on the kinetics of cathodic deposition of mercury-soluble metals on corresponding amalgams. The results obtained by kinetic studies of reactions of exchange of metallic ions between diluted amalgams and nitrate solutions indicate that the exchange current decreases in the following order:

$$\text{Tl, Pb, Cd} > \text{Cu, Zn} > \text{Ni}$$

The potential-time curves obtained by Heyrovsky by means of oscillographic polarography show that the degree of reversibility of the discharge and ionization reactions at mercury (more precisely, amalgam) electrodes decreases in the following sequence:

$$\text{Tl, Pb, Cd, Sn, Bi, Sb, Zn, Cu}$$

The order of arrangement of metals according to the degree of their irreversibility and, hence, to the magnitude of metal overpotential is practically independent of whether a metal is deposited on a solid cathode of the same metal or on a diluted amalgam of the corresponding metal. The deposition of metals of the iron group on mercury is also accompanied by a polarization considerably higher than in the case of all the other metals listed in Table 22.1. Here it proceeds still less reversibly than on solid cathodes. These metals however are almost incapable of forming amalgams and they are deposited at mercury cathodes onto poorly bound small crystal islands.

22.2.2. THE EFFECT OF SOLUTION COMPOSITION

Systematic investigations of the effect of the solution composition on the kinetics of electrodeposition of metals were begun in 1917 by Izgaryshev. It was found that the cathodic deposition of metals from solutions of their simple salts is affected by the nature of the

salt anion. The effect of the anion on the overpotential and on the nature of the deposits formed is observed for many metals but it reveals itself most strongly in the case of metals the deposition of which does not involve high polarization. Usually the overpotential decreases from anion to anion in the following order:

$$PO_4^{3-},\ NO_3^-,\ SO_4^{2-},\ ClO_4^- > NH_2SO_3^- > Cl^- > Br^- > I^-$$

The tendency to form rougher, coarse-grained deposits increases in the order indicated. The effect of anions is quite comparable with the effects exerted by crystallographic factors. For example, when one changes from perchlorate solutions to sulphamine solutions an almost two-fold decrease of the overpotential is observed in the electrodeposition of lead, while in changing from the (111) face to (100) it decreases by less than one and a half times.

The presence of indifferent cations in the solution, apart from the discharging metallic ions, increases the metal overpotential. Such effects have been observed in the deposition of nickel, zinc, copper, and other metals. Indifferent cations in aqueous solutions are usually hydrogen ions. As a general rule, the metal overpotential rises with increasing concentration of hydrogen ions. The overpotential is found to increase considerably in the presence of surface-active cations of the tetrasubstituted ammonium type.

The high sensitivity of the process of metal electrodeposition to the presence of impurities in solutions indicates that the addition of any substances (not only electrolytes), especially those having surface-active properties, is essential here. By way of example, the introduction of a negligible amount of gelatine (of the order of 0.005%) into a plating bath changes the cathode polarization and the nature of the deposits formed (Izgaryshev, Titov, 1917).

The addition of traces of molecular and ionic substances to the solution is one of the most effective ways for altering the course of the electrodeposition of metals. Many predominantly organic substances are capable of enhancing the lustre of dull deposits (brightening agents), levelling out their surfaces (smoothing agents) and modifying other properties, e.g., porosity, hardness, embrittlement, ability to occlude hydrogen, etc. (Kudryavtsev, Matulis, and others).

A new type of polarization for the cathodic deposition of metals discovered by Loshkarev is adsorption polarization, which alters the rate of metal deposition on mercury and also on solid cathodes after addition of certain surface-active substances (e.g., tribenzylamine). First, the deposition rate becomes slower than before addition of surface-active substances and, second, it becomes independent of the cathodic potential over a wide range of potentials. However, after a certain (usually, strongly negative) potential is reached, the effect of the additive ceases. The rate of deposition begins to

increase rapidly, approaching the normal value under given conditions, which corresponds to the diffusion limiting current. A comparison of the results obtained from polarization measurements on mercury cathodes with electrocapillary curves and differential capacity curves (traced before and after the additive is introduced) has shown that the potential, at which the action of the additive discontinues, coincides with the potential of its desorption (Fig. 22.4). The effect of the addition agent is specific here. One and the same addition agent (or a certain combination of additives) has a different retarding effect on the discharge of different ions on a mercury cathode. The phenomenon of adsorption polarization is used to improve the quality of deposits in the electrolytic production of alloys.

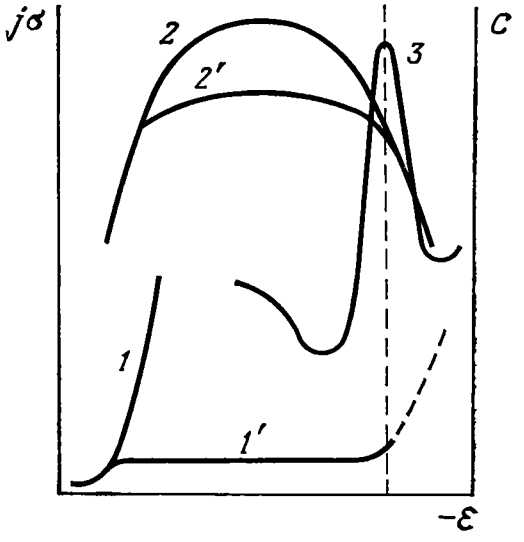


Fig. 22.4. Diagram illustrating the phenomenon of adsorption polarization (after Loshkarev):

1 and *1′*—polarization curves in the cathodic deposition of a metal under ordinary conditions and under the conditions of formation of an adsorption film; *2* and *2′*—electrocapillary curves traced in a pure solution and in a solution containing surface-active substances; *3*—capacity curve with a desorption peak

All these data refer to the deposition of metals from solutions of their simple salts. If inorganic or organic additives form complex compounds with the metal being deposited and convert its hydrated ions into complex ones, the course of the cathodic process will change markedly. First of all, the formation of complexes in the solution shifts the equilibrium potential of the metal in the negative direction by reducing the concentration of its free ions. The addition of a substance M′A (whose anions are capable of forming complex compounds MA_x with the ions of the metal being deposited, M^{z+}) causes a complex formation reaction in the solution:

$$M^{z+} + xA^- = MA_x^{z-x} \qquad (22.4)$$

where $(z - x)$ is the charge of the ions formed. Reaction (22.4) is characterized by the complex-formation constant (or formation constant):

$$K = \frac{[MA_x^{z-x}]}{[M^{z+}][A^-]^x} \qquad (22.5)$$

The reciprocal of this quantity is called the instability constant:

$$K_{in} = \frac{[M^{z+}][A^-]^x}{[MA_x^{z-x}]} \qquad (22.6)$$

The instability constant characterizes the ability of a complex to dissociate with recovery of the initial ions M^{z+} and thus determines their equilibrium concentration

$$[M^{z+}] = K_{in} \frac{[MA_x^{z-x}]}{[A^-]^x} \tag{22.7}$$

As a result of the complex formation reaction a certain fraction of the M^{z+} ions (which is the greater, the lower the instability constant) will be present as complex ions M_x^{z-x} in solution and, consequently, the concentration of free metallic ions must diminish. This decrease and, hence, the shift of the reversible electrode potential in the negative direction will be the greater the lower the instability constant and the higher the concentration of the addition agent. By choosing appropriate complexing agents and their concentrations one can change the equilibrium potentials of different metallic ions present in the solution so as to ensure either their codeposition to produce an alloy or their maximum possible separation.

The appearance of complexes in solution affects not only the equilibrium potentials of metals but also the magnitude of overpotential and the nature of cathodically formed deposits. On switching from simple electrolytes to complex ones the overpotential generally increases and the grain size of deposits decreases; simultaneously, the tendency toward the formation and growth of dendrites is suppressed. For example, silver, which is deposited at the cathode during electrolysis of its nitrate solution almost without polarization and gives course-grained rough deposits, can be obtained from complex cyanide electrolytes in the form of smooth fine-grained deposits.

22.3. THE NATURE OF METAL OVERPOTENTIAL

The electrode polarization observed in the deposition of metals may be associated either with phase transformations (see Chapter 15), in which case it is one of the types of phase overpotential (the slow formation of two- and three-dimensional nuclei, surface diffusion of adatoms or adions), or with the slow occurrence of the electrochemical step (see Chapter 16), in which case it may be identified with electrochemical overpotential. In the electrodeposition of metals, hindrances at the transport and chemical-transformation steps (see Chapter 16) preceding the electrochemical act play an important role. In considering the cathodic deposition of metals (especially, from complex electrolytes) it is therefore necessary to take into account concentration polarization, i.e., diffusion overpotential and chemical (or reaction) overpotential. And, finally, under the conditions of cathodic deposition of metals, the energy state of the ion in the deposit formed may differ from its state in the normal crystal

lattice of the given metal and correspond to a higher energy level. The transformation from this metastable form into a stable form may also cause the appearance of a special type of phase (crystallization) overpotential.

The predominance of one or other type of overpotential is governed by the nature of the metal, solution composition, current density, and electrolyte temperature. When simple, noncomplex electrolytes are used at ordinary temperatures, the overpotential depends on the nature of the metal (see Table 22.1). Experimental data indicate that the deposition of metals at the beginning of the series (Hg, Ag, Tl, Pb, Cd, Sn) is accompanied by insignificant polarization caused mainly by the slow formation and growth of a new phase. The slow rate of the electrochemical step is not essential here. In the electrochemical literature these metals characterized by phase overpotential are often called *normal metals*. Conversely, in the deposition of metals standing at the end of the series in Table 22.1 (metals of the iron group) a high polarization is observed, which is predominantly caused by the slow rate of the electrochemical step. These metals, characterized by an electrochemical overpotential, are called *inert metals*. Metals such as Bi, Cu, and Zn occupy an intermediate position with respect to both the magnitude of polarization and the nature of overpotential (here the superposition of several types of overpotential is most probable).

According to Volmer, the different nature of deposits cathodically formed by normal and inert metals is due to this difference in the magnitude and type of overpotential. From this point of view, all factors responsible for the slow rate of the discharge step must diminish the relative role of crystallization phenomena and encourage the formation of uniform and fine-grained deposits. The discharge reaction rate can be reduced still further either by conversion of simple ions into more stable complexes or through the addition of surface-active substances (if their adsorption has the strongest effect on the discharge step). This point of view is supported by the change in the structure of deposits observed in going from simple electrolytes to cyanide ones and also by the character of electrodeposition under the conditions of adsorption polarization.

22.4. FACTORS CONTROLLING POLARIZATION IN THE CATHODIC DEPOSITION OF VARIOUS METALS

22.4.1. THE ENERGY OF THE ION IN A METAL AND ITS STATE IN SOLUTION

It is not quite clear yet why there is such a marked difference in the magnitude and nature of overpotential of normal and inert metals and which properties of metals (or solutions) are responsible

for it. An attempt was made to ascribe these phenomena to the difference in the bond strength of ions in solution and in the crystal lattice of normal and inert metals. This assumption is tantamount to postulating that the ions participating in the discharge are in the same form in which they are present in solution and that the discharge moves the ion directly to its final position in the metal lattice. According to this assumption the discharge act coincides with the overall electrode reaction of metal deposition, and the energy changes involved correspond to the Gurney diagram (see Fig. 9.8, page 235). The minimum of the left potential curve represents the stable position of the ion in solution and, in the case of simple ions, is determined by the hydration heat H of the ion. The minimum of the right potential curve refers to the stable position of the ion in the surface layer of the metal lattice and is determined by the work of its removal Y. The activation energy of discharge increases with increasing hydration energy of the ion and with decreasing work of its removal. Thus it would be expected that for normal metals the hydration energy of their ions in solution is lower, and the work of removal of the ions from the lattice greater, than for inert metals. This assumption however is not confirmed by experimental data. For example, from Table 22.3 it follows that the

TABLE 22.3

Comparison of Chemical Energies of Hydration with Energies of Removal of Ions from the Crystal Lattice for Some Metals

Property, kcal/g-ion	Ions							
	Ag^+	Cd^{2+}	Co^{2+}	Cu^{2+}	Fe^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
H	113	425	480	491	448	491	353	479
Y	131	432	409	535	430	472	371	460
$H-Y$	−19	−7	+71	−44	+18	+11	−18	+19

difference $H - Y$, as well as the absolute values of the hydration energy and the work of ion removal, is almost identical for zinc and nickel, though zinc is deposited with a much lower overpotential than nickel.

The inadequacy of such a simplified picture follows from more general considerations as well. Standard electrode potentials vary along with the variation of the difference between the chemical hydration energy of ions in solution and the work required to remove the ions from the crystal lattice. It would have seemed therefore that

the metal overpotential must vary in the same sequence as the voltage series of metals. But this conclusion is in discord with experiment. For example, zinc, whose standard potential is equal to —0.76 V, is deposited with a lower overpotential than iron, the standard potential of which is —0.44 V. At the same time the overpotential in the deposition of zinc is approximately the same as in the deposition of copper, which is an electropositive metal ($\varepsilon^0_{Cu^{2}/Cu} = +0.34$ V). This by no means implies that the ionic bond strength in solution and in the metal plays no part at all. This factor however cannot be estimated simply by comparing the values of H and Y.

The assumption that the deposition of a metal proceeds not as a multistep consecutive reaction but as a single elementary act contradicts all data obtained in studies of the kinetics of various electrochemical processes. This assumption would imply, say for cathodic hydrogen evolution, that the hydrogen overpotential is independent of the nature of the metal, which is not true. In order to explain the relation existing between the metal overpotential and the nature of the metal and also the effect of the solution composition on overpotential, it is necessary to take into account not only the initial and final states of metallic ions but also the nature of elementary acts. Here one should reckon with the state and properties of reacting particles at various stages of the overall process.

Many investigators attempted to improve the theory of metal electrodeposition by resorting to the concepts of the electronic structure of metallic ions. One such attempt was made by Lyons (1954). According to this author, the metal overpotential depends on the electronic structures of discharging ions and of the cathodically deposited metal. Here the overpotential is assumed to be especially high in two cases. First, if aquo-complexes (or other complexes) are formed by ions at the expense of the electrons located in inner orbitals (inner-orbital complexes), which results in the formation of the strongest ionic bonds in solution. Second, if the difference in the electronic structure of the ion and the metal is great; in this case a considerable activation energy is required for these structures to be rearranged during discharge. Discharging ions usually have a different structure than the ions present in solution. This is attributed to the partial dissociation of a simple hydrated or a complex ion on the electrode during adsorption. The available bonds hold the ion on the electrode surface, while the electronic structure of the ion is further rearranged, up to the moment of discharge, tending to assume the structure of the ion in the metal. This is followed by the discharge involving either complete dehydration of the ion or decomposition of the complex and inclusion of the metal atom into the crystal lattice.

All the metals listed in Table 22.1 form, according to Lyons, outer-orbital aquo-complexes, i.e., complexes formed with the parti-

cipation of electrons situated in outer orbitals. This makes possible their deposition from aqueous solutions in contrast to such metals as titanium, zirconium and others, whose ions are present in solution in the form of inner-orbital complexes. The high overpotential of metals belonging to the iron group is attributed to a considerable difference in the electronic structure of discharging aquo-ions and the corresponding metal. Conversely, the electronic structure of normal metals in a crystal and in aquo-complexes is similar and therefore they have a low overpotential.

Lyons' views reflect, to some extent, certain features characteristic of the processes of cathodic metal deposition. No doubt, the electronic structure of ions has some share in these processes. At the same time the Lyons theory does not give a detailed explanation of the nature of metal electrodeposition processes. This is associated, first of all, with the lack of reliable data on the structure of ions in solution and at the electrode surface, which makes one resort to hypothetical structures. Further, the Lyons theory, though making use of such hypothetical structures, is incapable of explaining certain experimental relations concerning, for example, the deposition of metals of the platinum group. This theory does not take into account the effect of the electrode potential and of the double-layer structure on the electrodeposition of metals. And, finally, it cannot explain the role played in this process by the solution composition and, especially, by surface-active substances. The concepts of the role of the structure of discharging metallic ions in the electrodeposition of metals were further developed by Vlček (1957).

22.4.2. THE ACTIVITY OF THE CATHODE SURFACE IN METAL DEPOSITION

According to another point of view the nature and magnitude of metal overpotential depend on the state of the cathode surface, which may be different for different metals. One of the causes responsible for this difference is associated with the possibility of hydrogen evolution and its influence on the course of metal deposition. It is known that electrolytic deposits of iron, nickel and cobalt always contain a noticeable amount of hydrogen. The presence of hydrogen may be regarded as one of the possible factors causing distortion in the crystal lattice of deposits of these metals, internal stresses, embrittlement, etc. Deposits of copper and zinc contain less hydrogen. Hydrogen is practically undetectable in electrolytically deposited cadmium or lead. From this it follows that the metal overpotential increases with increasing amount of hydrogen included in a metal deposit, i.e., that hydrogen probably interferes with the cathodic deposition of metals. It was thought that hydrogen has an inhibiting

effect on the discharge process by forming a surface film or metal hydrides.

In connection with the effect of hydrogen on the kinetics of metal deposition it is important to find out the factors responsible for the presence of different amounts of hydrogen in different metals and hence for the difference in the inhibiting effect. It has been found that, in a general case, there is no direct relation between the fraction of the total current consumed for hydrogen evolution and the hydrogen content in the metal. For example, in the electrodeposition of zinc the current yield of hydrogen is usually higher than in the case of iron; but the content of hydrogen in it is always lower and the overpotential at which hydrogen is evolved on it is also lower. The deposition overpotential of metals increases in the same order in which their hydrogen overpotential decreases. However, the important point is the mechanism of hydrogen evolution on a given metal rather than the magnitude of hydrogen overpotential (Antropov, 1952). The occlusion of hydrogen by a metal deposit is the more probable the slower the removal of adsorbed hydrogen atoms from the metal surface. The largest amounts of hydrogen are therefore detected in cathodic deposits of metals belonging to the iron group since in this case the recombination of hydrogen atoms proceeds at a slow rate.

The presence of adsorbed or occluded hydrogen however cannot be considered as the main factor determining the specificity of the cathodic deposition of metals.

The difference in metal overpotential and in the nature of cathodic deposits might be attributed to the different tendency of metals towards passivation and their different adsorption capacity. The appearance of foreign substances on the surface of a growing deposit impedes the discharge of metallic ions and their incorporation into the crystal lattice. This retarding effect must be the more pronounced, the more readily a given metal is passivated. The role of passivating agents can be played by dissolved oxygen, impurities of organic substances and catalytic poisons, certain foreign (indifferent) ions which do not participate in the electrode reaction, and other substances. From this point of view, the special position of metals of the iron group, in particular their high metal overpotential, is due to the fact that these metals exhibit a stronger tendency toward passivation (Samartsev, Gorbunova, Vagramyan).

This factor however does not seem to be decisive either and evidently is not responsible for the order of arrangement of metals according to their overpotential. The difference in the metal overpotentials of inert and normal metals remains large even when solutions are most thoroughly freed from impurities and oxygen. Similarly, lead, which is passivated much more readily than zinc, is deposited at a lower overpotential.

22.4.3. THE CHARGE OF THE METAL SURFACE IN CATHODIC DEPOSITION

The occurrence of adsorption phenomena at a metal-electrolyte interface and, consequently, the degree of their effect on the processes taking place there largely depend on the potential or, more exactly, on the charge of the metal.

In the past it was taken for granted that the cathode surface is always negative, and the more negative the less noble is the electrode metal. This point of view, which has survived up to now, is incorrect. The charge on the metal surface is determined neither by the role played by the metal in an electrochemical process (i.e., whether it is the cathode or the anode) nor by its electrode potential under given conditions. The charge on the electrode surface can be evaluated by using the correlative or φ-potential scale proposed by Antropov. The electrode potential on the φ scale is the difference between the potential of the electrode under the particular conditions (e.g., in the electrodeposition of metals) and the corresponding null point:

$$\varphi = \varepsilon - \varepsilon_N$$

The magnitude of the electrode potential on the φ scale serves as a measure of the surface charge, making it possible to predict which ions have more chance to be adsorbed under given conditions. This can be illustrated by the cathodic deposition of nickel, zinc, cadmium, and lead from solutions of their simple salts. All these metals are deposited at negative potentials (on the hydrogen scale), which, under ordinary electrolysis conditions, are approximately as follows: —0.80 V (Ni and Zn), —0.45 V (Cd) and —0.15 V (Pb). Their potentials on the correlative scale, i.e., their charges, can be estimated by using data on the null points of these metals (see Table 10.3):

$$\varphi_{Ni} = -0.80 - (-0.2) = -0.6 \text{ V}$$
$$\varphi_{Zn} = -0.80 - (-0.5) = -0.3 \text{ V}$$
$$\varphi_{Cd} = -0.45 - (-0.7) = +0.25 \text{ V}$$
$$\varphi_{Pb} = -0.15 - (-0.7) = +0.55 \text{ V}$$

From these values of φ potentials it follows that under the conditions of electrodeposition nickel has the most negative charge, then comes zinc, which is also negatively charged, while cadmium and lead are charged positively. In the course of electrodeposition, predominantly cations must be adsorbed on the surface of nickel and zinc deposits and anions on the surface of cadmium and lead deposits These conclusions apply only to solutions containing no surface-active substances capable of being adsorbed also on a like-charged metal surface. They however can also be extended to solutions containing surface-active substances, provided that the specificity of adsorp-

tion is determined by the properties of their particles and not of the metal. Then, knowing the mechanism of adsorption of surface-active substances at least on one metal, e.g. on mercury, one can find, by means of the correlative scale, the most probable region of potentials in which the same substances may be adsorbed on the surface of any other metal. This allows one to establish, in each particular case, the possibility of their influence on the kinetics of electrodeposition. Suppose a substance can be adsorbed on the surface of mercury up to the potential ${}_{Hg}\varepsilon_{des} = -1.0$ V, which may be called the negative desorption potential (the value of desorption potential on mercury can easily be found from capacity or electrocapillary measurements). Since the null point of mercury is -0.2 V, the negative desorption potential on the φ scale must be: ${}_{Hg}\varphi_{des} = -1.0 - (-0.2) = -0.8$ V. Assuming, as a first approximation, that desorption always begins at one and the same charge and using the properties of the φ scale, one can assert that for any metal M desorption will occur at a value of ${}_{M}\varphi_{des}$, equal to ${}_{Hg}\varphi_{des}$, i.e.,

$$ {}_{M_1}\varphi_{des} = {}_{M_2}\varphi_{des} = \ldots = {}_{Hg}\varphi_{des} $$

Hence, the given surface-active substance will cease affecting the kinetics of an electrode process at one and the same φ potential irrespective of the nature of the metal. To a constant φ potential of desorption of the given substance there will, however, correspond entirely different electrode potentials dependent on the nature of the metal. For example, the substance chosen will be desorbed from the zinc surface at a ε potential equal to -1.3 V and not to -0.8 V (as in the case of mercury) since

$$ {}_{Zn}\varphi_{des} = {}_{Hg}\varphi_{des} = {}_{Zn}\varepsilon_{des} - {}_{Zn}\varepsilon_{N} $$

and

$$ {}_{Zn}\varepsilon_{des} = {}_{Zn}\varphi_{des} + {}_{Zn}\varepsilon_{N} = {}_{Hg}\varphi_{des} - {}_{Zn}\varepsilon_{N} $$

Analogously, it can be shown that the desorption potentials for cadmium and lead will be the same (-1.5 V). In just the same way one can find the potentials at which adsorption begins or, in other words, the positive potentials of desorption. Having thus determined the range of ε potentials within which the adsorption of the given substance on different metals is probable, one can establish whether it is capable of affecting a particular electrochemical reaction proceeding at a specified electrode potential.

For polycrystalline metals the region of reversible adsorption may be wider than for mercury since the faces of the same crystal with different crystallographic indices are characterized by different work functions and, hence, by different null points. In practice, however, the opposite effect is often observed—the region of potentials in which adsorption occurs at solid metals under the conditions of their electrodeposition is found to be narrower than that determi-

ned from the data of electrocapillary or capacity measurements on mercury. The point is that in the electrodeposition of metals surface-active substances are either incorporated into the cathodic deposit or subjected to chemical change, i.e., are consumed in some way or other at a certain rate during electrolysis, and their adsorption ceases to be reversible. The loss of the surface-active substance in the catholyte must be constantly compensated, and here diffusion becomes important. If the kinetics of adsorption are partly controlled by diffusion (diffusion-adsorption control), the concentration of surface-active substances near the cathode will be lower than that in the bulk of the solution. In this case, a more or less correct picture of the adsorption region can be obtained by using the electrocapillary curve traced in the solution and the bulk concentration of the additive equal to that set up near the cathode surface during the electrodeposition of a metal.

If surface-active substances are supplied to the growing cathodic deposit at a limiting current (pure diffusion control), their electrocapillary behaviour will play but a minor role.

Nonetheless, the considerations based on the correlative scale of potentials may be useful in searching for effective additives and electrolytes to be used in plating and hydroelectrometallurgical baths.

Since the charge of the metal surface determines the conditions of adsorption at the metal-solution interface, it must also be associated with the magnitude of metal overpotential. If the charge of a metal is positive ($\varphi > 0$) with respect to the solution, then the double-layer sheet on the solution side will consist primarily of anions. Conversely, if the metal is charged negatively ($\varphi < 0$), predominantly positive ions will be attracted to its surface from the solution side. The former case is exemplified by silver in silver nitrate solutions, and the latter by zinc in zinc sulphate solutions. Indeed, if it is assumed that the ionic activity of each of these metals is equal to unity, then their ε potentials will correspond to standard values and their φ potentials will be as follows:

$$_{Ag}\varphi = {}_{Ag}\varphi^0 = {}_{Ag}\varepsilon^0 - {}_{Ag}\varepsilon_N = 0.8 - (-0.4) = 1.2\,V$$

and

$$_{Zn}\varphi = {}_{Zn}\varphi^0 = {}_{Zn}\varepsilon^0 - {}_{Zn}\varepsilon_N = -0.76 - (-0.5) = -0.26\,V$$

Suppose that corresponding metals are deposited on these electrodes. In the first case (i.e., in the deposition of silver) the discharge of positive ions is facilitated by the attractive forces operating between these ions and the anions adsorbed on the cathode in the same way as a positively charged grid accelerates the movement of electrons in a three-electrode valve. At a small shift of the potential to the

negative side the rate of discharge will be considerable. Therefore, even at high current densities the overpotential remains low. In the second case (i.e., the deposition of zinc) not only is the accelerating effect of anions absent, but foreign cations may even exert an inhibiting effect if they are present in solution together with zinc ions. The cause for the appearance of this inhibiting effect can be easily understood if one takes into account that at the moment of application of a current metallic ions and foreign cations, e.g., hydrogen ions, are present in the double layer. When the current is switched on, the ions of the metal (when its deposition is the principal cathodic process) begin to discharge and their concentration in the double layer will diminish, while the number of indifferent cations will remain constant because they are not discharged. The loss of positive charges must be compensated by the supply of new cations to the double layer; these new cations may be either metallic ions or indifferent cations. Thus, when the potential is shifted to the negative side (i.e., when the negative charge on the metal surface increases), the fraction of discharging cations in the double layer will be reduced, while the quantity of indifferent cations and the net positive charge of the cationic sheet will increase. The supply of metallic cations will thus be hampered, and a higher overpotential will be required for the discharge process to occur. When complex anions are discharged, which is probably the case with cyanide electrolytes in silver- and zinc-plating processes, the situation is reversed. Here the anionic sheet will exert a retarding rather than activating effect.

The existence of such effects is confirmed by experimental facts (decrease of metal overpotential with increasing surface activity of a metal salt anion; its rise with increasing concentration of hydrogen ions and upon addition of surface-active cations; a sharp increase in hydrogen overpotential in going from a positively to a negatively charged metal surface, etc.). All normal metals (Hg, Ag, Tl, Pb, Cd), which are deposited at a negligibly low overpotential, are charged positively with respect to solutions of their simple salts ($\varphi > 0$), and all metals, the deposition of which is accompanied by high overpotential (metals of the iron group) are charged negatively ($\varphi < 0$). That is why in the electrodeposition of metals it is necessary to take into account the charge on the electrode surface, even though it does not determine all the specific features of these processes. For example, the large difference in overpotential in the deposition of zinc and nickel, metals that possess approximately equal negative surface charges under equilibrium conditions, has not yet been accounted for. Similarly, the deposition of copper should proceed, judging by the value of its φ potential, just as easily as the deposition of cadmium or lead, but this does not agree with experimental data.

22.4.4. OTHER POSSIBLE CAUSES OF METAL OVERPOTENTIAL

Since it is impossible to explain all the kinetic peculiarities of the electrodeposition of metals from a single general point of view, one has to search new ways for interpreting this process and make assumptions specifically for describing concrete reactions. For example, there is an opinion that the overpotential in metal deposition is associated with the number of electrons participating in the elementary discharge act (Heyrovsky). It is assumed here that one-electron reactions proceed practically unhindered. In all cases where only one electron takes part in the discharge act (or when the process may be broken down into a number of successive one-electron steps) the overpotential must be low. Conversely, if two electrons participate simultaneously in the discharge of metallic ions, a high metal overpotential should be expected. According to these concepts, the low overpotential observed in the deposition of thallium and silver is associated with the fact that the reduction process requires the participation of one electron:

$$Tl^+ + e = Tl$$
$$Ag^+ + e = Ag$$

The low metal overpotential characteristic of copper and zinc is accounted for by the possibility of discharge in two one-electron steps:

$$Cu^{2+} + e = Cu^+$$
$$Cu^+ + e = Cu$$

and

$$Zn^{2+} + e = Zn^+$$
$$Zn^+ + e = Zn$$

For metals of the iron group the discharge proceeds with the simultaneous addition of two electrons

$$Fe^{2+} + 2e = Fe$$

this being responsible for the slow rate of this process (the probability of simultaneous addition of two electrons is low) and the high overpotential.

It has long been known however that the rate of electrodeposition and also of electrodissolution (see Chapter 23) of metals of the iron group depends on the solution pH and the presence of impurities. Burshtein, Kabanov and Frumkin (1947) postulated the direct participation of hydroxyl ions in the kinetics of these processes. In their opinion, OH^- ions function as a sort of a catalyst. The

mechanism of the cathodic deposition and anodic dissolution of iron, cobalt and nickel with the formation of intermediate particles of the type FeOH, $FeOH^+$ or $Fe \cdot FeOH^+$ was discussed later by Heisler, Bockris, Fischer and Lorenz, and by many other authors. Several schemes have been suggested to explain experimental data, in particular, the pH dependence of the reaction rate, the small slope of Tafel line in pure solutions of sulphuric acid, its increase in the case of hydrochloric acid solutions and on addition of surface-active substances, etc. The Bockris scheme is given below by way of illustration.

$$Fe^{2+} + OH^- = FeOH^+$$

$$FeOH^+ + e = FeOH$$

$$FeOH + e = Fe + OH^-$$

Here the entire process is split up into one chemical and two electrochemical steps, the rate of the overall reaction being determined by the transport of the first electron (the second step).

CHAPTER 23

Electrochemical Dissolution and Passivity of Metals

Electrochemical dissolution of metals includes two basic groups of processes: enforced dissolution on application of a current (or anodic dissolution of metals) and spontaneous dissolution as a result of chemical interaction with the surrounding medium. The spontaneous dissolution of a metal as well as its anodic dissolution are generally called corrosive destruction or corrosion of metals if these processes are undesirable. These two groups of processes have both common and specific characteristics; often they are found to occur simultaneously.

23.1. ANODIC DISSOLUTION OF METALS

23.1.1. GENERAL DESCRIPTION OF THE PROCESS

Metallic anodes are widely used in the electrochemical industry. The following requirements are to be met by anodes depending on the process involved.

1. An anode must dissolve quantitatively with the formation of aquo-ions (or complex ions) of only one valency. These requirements must be met in the production of certain electrodeposited coatings, for example, in copper-plating, nickel-plating or zinc-plating processes. If a copper-plating process is conducted in acidic baths, it is necessary that copper be dissolved and pass into solution as bivalent ions. The reaction

$$Cu = Cu^{+} + e$$

is undesirable here since the accumulation of univalent ions of copper in excess of the equilibrium concentration leads to the deposition of metallic copper in the form of powder in consequence of the disproportionation process:

$$2Cu^{+} = Cu + Cu^{2+}$$

In the presence of such powder, which finds its way to the cathode surface, rough deposits are produced instead of smooth ones (as required for electroplating).

2. The dissolution of anodes must be selective, i.e., one of the components of the anode material is to dissolve quantitatively (often in the form of definite ions), while the others must not dissolve at all. An example is the electrolytic refining of copper. In this process copper dissolves as cupric ions, while noble metals remain intact and accumulate at the bottom of the bath in the form of so-called sludge.

3. An anode must dissolve to give coherent solid products of the interaction of its ions with the other ions present in the solution or with anodically evolved oxygen. Examples are the anodizing of aluminium, the bluing of steel, the charging of the positive pole of a lead accumulator, phosphating.

4. An anode must dissolve with the simultaneous smoothing and brightening of the surface (electropolishing). It need not dissolve quantitatively in this case and part of the current may be consumed for oxygen evolution.

5. An anode must not dissolve at all, and the only electrode process must be the evolution of a gas, most frequently oxygen. This requirement must be met in the electrolysis of water, electrowinning of zinc, chrome-plating, and also in the electrolysis of solutions of alkali metal chlorides. In the latter case, the anode must provide, apart from stability, the predominant evolution of chlorine, and impede oxygen evolution.

If, under the influence of an external current, the amount of dissolved metal is greater than would be expected on the basis of Faraday's laws, it will mean that the anodic dissolution of the metal is accompanied by its spontaneous dissolution, i.e., the metal is simultaneously subjected to corrosion. If the anode, which must be stable under the given conditions, in fact dissolves as a result of either the application of an external current or the interaction with the surrounding medium, this will indicate the simultaneous occurrence of anodic dissolution and corrosion.

Which of these cases of the anodic behaviour of metals will actually occur depends on the nature of the metal itself and on the composition of the solution, in particular on its pH. Current density and temperature are also important here. The same metal may behave either as a soluble or as a stable anode, depending on the particular conditions.

The probable behaviour of each metal can be estimated by using potential-pH diagrams (*Pourbaix diagrams*). They enable one to establish the thermodynamically most probable regions of potentials, pH and concentrations of metallic ions corresponding to the different electrochemical behaviour of a given metal. For example, from the potential-pH diagram for zinc (Fig. 23.1) it can be seen that in the region of acidic solutions at potentials above the straight line *1* zinc dissolves to yield hydrated ions Zn^{2+}_{aq}. When a pH value

of 6.5 is reached, sparingly soluble zinc hydroxide $Zn(OH)_2$ may be formed and the dissolution of zinc is hindered. The hydroxide region is limited by straight lines *2*, *3*, and *4*. At pH = 14 zinc will again readily pass into solution, this time as anions $ZnO_{2(aq)}^{2-}$, which are readily soluble in alkaline solutions and do not impede the anodic dissolution of zinc or its corrosion. This region is limited by straight lines *4* and *5* and the ordinate axis. Below the broken line *1-3-5* is the region of stability of zinc, where its dissolution

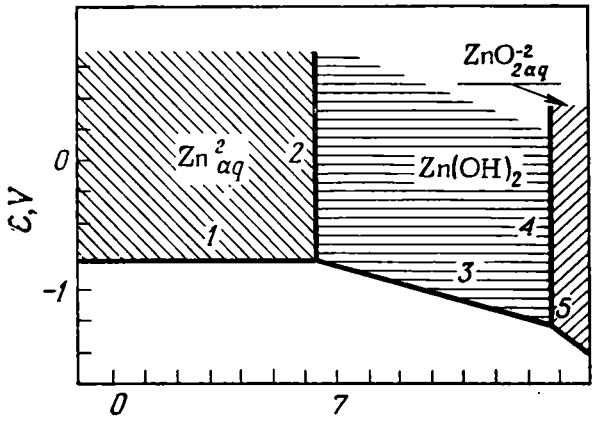


Fig. 23.1. Pourbaix diagram for zinc

is thermodynamically improbable. The potential-pH diagram in Fig. 23.1 refers to the special case where the activity of zinc ions in solution is 10^{-2} mole/litre. At a different activity the disposition of the regions will change somewhat. Pourbaix and his colleagues plotted potential-pH diagrams for most metals and a number of alloys for four activities of metallic ions (1, 10^{-2}, 10^{-4}, and 10^{-6} mole/litre).

23.1.2. ANODIC DISSOLUTION OF METALS WITH FORMATION OF READILY SOLUBLE COMPOUNDS

The anodic dissolution of a metal, in which metal passes into solution as simple hydrated ions or as complex ions is in many respects the reverse of the cathodic deposition of metals. In the case of simple hydrated ions, the overall reaction of anodic dissolution may be written in the form of the equation

$$[M] + xH_2O = M^{z+} \cdot xH_2O + ze \qquad (23.1)$$

and for complex ions the overall reaction is

$$[M] + xA^- + yH_2O = MA_x^{z-x} \cdot yH_2O + ze \qquad (23.2)$$

In contrast to the cathodic deposition of metals, the anode process begins with the destruction of the crystal lattice of a metal and ends with the formation of metallic ions in solution. The direction of each individual step is also reversed. For example, the destruction of the crystal lattice of a metal replaces its formation, and the ionization of metal atoms replaces the discharge of ions, etc.

Metals are anodically dissolved usually at potentials more positive than the correspoding equilibrium potentials, i.e., their dissolution is accompanied by anodic polarization. The value of polarization can be determined by the equation

$$\Delta\varepsilon = {}_a\varepsilon_i - \varepsilon_r \qquad (23.3)$$

where ${}_a\varepsilon_i$ is the potential of the metal under the conditions of anodic dissolution at a current density i.

Anodic polarization may be ascribed to the slow occurrence of the transport, solid-phase destruction or ionization step. In the cathodic deposition of metals the slow transport step, i.e., the insufficient initial rate of transport to the electrode of the ions to be discharged, shifts the electrode potential in the negative direction. In the anodic dissolution process, the slow rate of the removal step results in the accumulation of the formed metallic ions near the electrode and, accordingly, displaces its potential to the positive side.

An analogous situation is also observed when any other step is slow. In view of this, at not-too-large deviations from the equilibrium state, a certain symmetry is observed in the cathodic deposition and anodic dissolution processes. For example, the anodic polarization of mercury, silver, thallium and cadmium is found to be close in magnitude to the cathodic polarization of the same metals at equal cathodic and anodic current densities, i.e., at equal rates of deposition and dissolution. Likewise, the variation of the anodic and cathodic overpotentials with increasing current density obeys approximately the same law for these metals.

A similar analogy is observed in the character of change of the metal surface during deposition and dissolution.

The energy of removal of a single structural unit of the crystal lattice depends on the site which it occupies on the crystal surface (Fig. 23.2). The most weakly bonded structural units are those located at the corners of the crystal, where each of them is surrounded by only three nearest neighbours. The passage of such a structural unit from the crystal lattice into solution is effected easily also because the largest number of water molecules can approach it since three of its sides face the solution. For a structural unit to be removed from a crystal edge the bond energy of four nearest neighbours has to be overcome, and from any point on the crystal face, five neighbours. The possibilities of contact with water molecules and, hence, of attractive forces being exerted by them are also more

limited in these cases. The anodic dissolution of perfect crystals begins therefore from the corners and edges of a crystal and gives rise to surface formations similar to two-dimensional nuclei. Just as in the case of cathodic deposition of a metal, its anodic dissolution is favoured by the presence of defects and disturbances in the lattice structure, including dislocations.

The similarity in the behaviour of normal metals during their cathodic deposition and anodic dissolution is also revealed with respect to effects associated with the composition of the solution. The activating effect of surface-active anions and the inhibiting

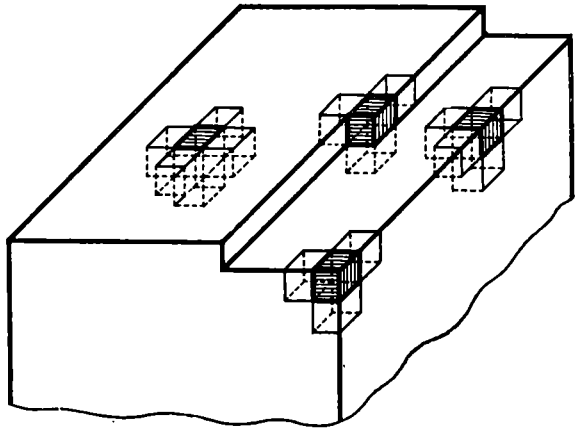


Fig. 23.2. Model of a dissolving crystal face showing energetically nonequivalent positions of a structural unit of the lattice

effect of foreign cations are also observed in the anodic dissolution process. But in this case the effect of anions is stonger and that of cations weaker than in the cathodic process.

For metals such as copper and zinc the symmetry of anodic and cathodic processes is manifested in a lesser degree. Their anodic dissolution usually proceeds more easily than their cathodic deposition.

A still larger difference is observed in the case of inert metals. The anodic polarization in the dissolution of the Fe-group metals is appreciably weaker than their cathodic polarization (at the same current density). Nevertheless, here too it reaches several tenths of a volt and considerably exceeds the anodic polarization associated with the dissolution of intermediate and normal metals. The sequence of metals arranged according to increasing metal overpotential (see Table 22.1, page 481) thus reflects also the order of increasing polarization in their anodic dissolution.

The behaviour of metals during anodic dissolution has not been studied so completely as their cathodic deposition. The experimental data obtained so far still indicate the applicability of the basic

concepts of the theory of electrochemical overpotential to metals of the Fe group. For instance, the kinetics of anodic dissolution of iron and nickel are described by Tafel's formula:

$$\eta_a = a_a + b_a \log i \tag{23.4}$$

which can easily be obtained from Eq. (16.68) if the rate of the discharge reaction is ignored compared with the ionization rate.

Experimental Tafel slopes are not always in agreement with the theory of slow discharge. For example, the coefficient b_a for the dissolution of iron in sulphuric acid solutions is only about 0.03.

If it is assumed that iron is dissolved anodically as ferrous ions (the most probable process), then the coefficient α, calculated from the equation

$$b_a = 2.303 \frac{RT}{2\alpha F} = \frac{0.06}{2\alpha}$$

is found to be equal to unity. This value of α is difficult to explain from the standpoint of the slow-discharge theory without assuming that the detachment of electrons occurs as a two-step consecutive process.

Apart from the transfer of electrons, the overall reaction of anodic dissolution of iron and, evidently, of other metals of the Fe group includes pure chemical steps involving anions, primarily hydroxyl ions, which catalytically accelerate the anodic process. The dissolution of iron in concentrated sulphuric acid solutions may be described, for example, by the following scheme:

$$\mathrm{Fe} + \mathrm{OH}^- = \mathrm{FeOH}_{ads} + e$$

$$\mathrm{FeOH}_{ads} = \mathrm{FeOH}^+_{ads} + e$$

$$\mathrm{FeOH}^+_{ads} + n\mathrm{H_2O} = \mathrm{Fe} \cdot n\mathrm{H_2O}^{2+} + \mathrm{OH}^-$$

where the second step determines the rate of the overall process.

There are a large number of experimental data which indicate that the anodic dissolution of other metals also involves OH^- ions, though the chemical polarization in the anodic dissolution of normal metals is probably determined mainly by the destruction of the crystal lattice.

The kinetics of anodic dissolution of metals must depend not only on the concentration of hydroxyl ions but on the anionic composition of the solution in general. It was usually assumed that other anions are capable, in a greater or lesser degree, of displacing OH^- ions from the surface of the metal being dissolved and thus reducing their catalytic effect. This point of view is borne out, for example, by the fact that the rate of iron dissolution decreases in going from sulphate to chloride solutions with the same pH value.

The surface activity of Cl^- ions is higher than that of SO_4^{2-} or HSO_4^- ions and Cl^- ions displace a larger number of OH^- ions, i.e., reduce more noticeably their catalytic effect on the dissolution process. However, it was shown by Kolotyrkin and coworkers that, in a more general case, any anions, like OH^- ions, are capable of catalyzing the anodic dissolution of metals. The net effect is therefore determined by the particular conditions of dissolution. In the region of small pH values, where the concentration of hydroxyl ions is low and the coverage of the surface of the metal being dissolved with these ions is insignificant, other anions, say, sulphuric acid anions, may be adsorbed on free sites of the surface without reducing the surface concentration of hydroxyl ions. Under these conditions the rate of dissolution must increase with increasing total concentration of anions. At high pH values when the concentration of OH^- ions and the surface coverage are high, the effect of displacement of hydroxyl ions by other anions becomes predominant and the dissolution rate may decrease with increasing total concentration of anions.

23.2. THE PASSIVITY OF METALS

23.2.1. GENERAL CHARACTERISTICS OF THE PASSIVE STATE OF METALS

A metal dissolving under the influence of anodic polarization may lose this ability if the conditions are changed and thus become an insoluble anode. This transformation of a soluble anode to an insoluble one is a special case of the passivation (or passivity) of metals. The phenomenon of metal passivation was discovered by Lomonosov and described in "Dissertation on the action of chemical solvents in general" (1738). Lomonosov noted that iron acted upon by a concentrated solution of nitric acid ceased to dissolve. Ever since the passivity of metals is understood to mean their ability to assume such a state in which they no longer participate in processes which are ordinarily typical of and thermodynamically possible for them.

The passivation of a metal is achieved not only through the action of corresponding oxidizing agents (an example being the passivation of iron by a concentrated solution of nitric acid). Metals can be passivated by other methods as well, for example, by anodic polarization. This phenomenon is most readily detected on potentiostatic curves of anode potential versus current density. One typical potentiostatic curve is given in Fig. 23.3. In the region of potentials not too distant from the equilibrium or stationary potential of a metal under given conditions, the rate of dissolution of the metal with the formation of its ions is found to increase as the potential is shifted in the positive direction. This region of potentials corre-

sponds to the active state of the metal, where it behaves as a soluble anode. When a certain value of potential (more positive than the initial value) is reached, the current density falls abruptly, which indicates that the dissolution process has suddenly become sluggish. In a rather wide range of potentials the current density and, hence, the rate of dissolution are almost constant and very low. This region of potentials corresponds to the passive state. The portion of the potentiostatic polarization curve connecting the active-state region

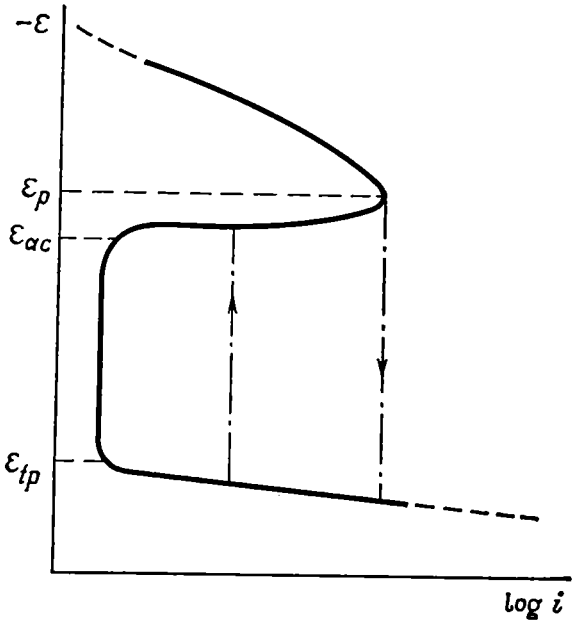


Fig. 23.3. Anodic potentiostatic curve for a metal capable of passivation

and the passivity region represents the transient or prepassivating state. As the potential becomes still more positive, the current density may rise again and the dissolution proceed at a faster rate. This region of potentials represents the transpassivity condition. It is usually characterized by the dissolution of a metal with the formation of ions of higher valency than in the case of its dissolution in the active state. Thus, as the potential is shifted to more positive values, the metal passes successively from the active state through the transient (prepassivating), and passive states to transpassivity. By shifting the potential from positive back to negative values one can make the metal pass through the same states in reverse order. The points of transition from one state to another are the most important data for the description of a potentiostatic curve. The potential ε_p at which the metal begins to change from the active to the passive state is called the passivation potential. At a potential ε_{ac} the metal is already passive. But when this potential is shifted to the negative side even by a small amount, the passive metal

becomes depassivated or activated. The potential ε_{ac} is usually called the activation potential or the Flade potential (Flade was the first to describe it); the last term is also often used to describe the passivation potential ε_p. The next characteristic potential is the quantity ε_{tp}—the depassivation potential at which the metal passes from the passive state to transpassivity. Each of the regions of the potentiostatic curve lying between critical points is characterized by its own law of variation of the dissolution rate (the anodic current density) with potential. In the active-state region the shift of the potential to the positive side increases the rate of dissolution, i.e., the slope of the curve $di/d\varepsilon$ is greater than zero. When the prepassivating condition sets in, the rate of dissolution diminishes with increasing positive value of potential, and the slope $di/d\varepsilon$ is negative. When the metal is insoluble (passive), the rate of dissolution is practically independent of the potential, and the slope $di/d\varepsilon$ may be taken equal to zero. In the transpassivity state, just as in the active state, the dissolution rate increases with potential, but the slope is different in absolute value. It should be noted that the transpassivity region, i.e., the passage of the metal back to the active state and the increase of its rate of dissolution, is not always observed at sufficiently high positive potential. Nonetheless, in this case too, the current density is observed to rise after a certain potential value is reached. However, here it does not mean the resumption of the active state, but rather the beginning of oxygen evolution. There are also cases where transpassivity is followed by a second passivity region, which may then be replaced by a new rise of current density associated with the dissolution of the metal (this time, with the formation of other ions) or with oxygen evolution.

The detailed demarcation of the regions corresponding to different states of a metal became possible owing to the use of the potentiostatic method of tracing polarization curves. When the galvanostatic method was used, many features of the anodic behaviour of metals escaped observation. Only abrupt changes of the potential could be detected, which, in the forward (from low to high current densities) and reverse (from high to low current densities) tracing of polarization curves, occurred at different current densities, indicating the existence of certain hysteresis phenomena (shown in Fig. 23.3 by dash-and-dot lines with arrowheads). However, long before the potentiostatic method was developed, Kistyakovsky (1910) proposed, on the basis of indirect data, a scheme of possible states of a metal, which largely coincides with that accepted at present.

The basic regularities of the passage of metals to different states were studied and described almost simultaneously by many authors. Mention should be made of the work by Akimov, Batrakov, Toma-

shov, Kolotyrkin, Prazek, Bonhoeffer, Franck, Stern, Edelanu, Okamoto, and other scientists. The transpassivity of metals was first treated in detail by Batrakov (1953) and Tomashov (1954). Based on the earlier observations by Akimov and Batrakov, Kolotyrkin for the first time traced a full potentiostatic curve and proved experimentally that all state transitions of the metal (Fig. 23.3) can be effected either by its polarization or by introducing into the solution various oxidizing agents capable of providing the corresponding potentials. The peculiarities of the behaviour of metals under the conditions of their anodic polarization appear thus to be intimately connected with the phenomena of passivity and transpassivity.

23.2.2. THE FILM AND ADSORPTION THEORIES OF PASSIVITY

Data obtained so far only partly characterize the active, passive and transpassive states and determine the conditions where each of these states can be attained. They yield no information concerning the cause of the passage of a metal from the active to the passive state and from the passive to the transpassive state. Two theories have been suggested to account for the phenomenon of passivity—the film theory and the adsorption theory. In the film theory (Kistyakovsky), which owes its origin to Faraday, it is assumed that the passivation of a metal is caused by the formation of a thin, usually oxide, film on the surface of the metal, which ceases to interact with the surrounding medium and is thus protected from dissolving. This oxide film has a thickness of several molecular layers and it may be regarded as a phase oxide. The more perfect the structure of the oxide film and the less the number of cracks and defects, the more complete is the passivation and the lower the rate of metal dissolution. The validity of the film theory is proved, for example, by the fact that for many metals, e.g. copper, lead, silver and platinum, the passivation (ε_p) and activation (ε_{ac}) potentials lie on either side of the reversible potentials of the corresponding metal-oxide electrodes. Likewise, the form of the dependence of passivation potential on the solution acidity often (for the above metals as well) corresponds to the pH variation of the potential of a metal electrode of the second kind:

$$\varepsilon_p = \varepsilon_p^0 - 0.06\ \mathrm{pH}$$

There are many cases, however, where the value of passivation potential cannot be related to the formation of any one of the known oxides of a metal. For example, for iron the passivation potential $\varepsilon_p = +0.58$ V, whereas the most positive of all the possible potentials of iron-oxide electrodes corresponding to the system Fe, FeO, Fe_2O_3 is only 0.22 V. Since the iron electrode is here the anode,

this difference, one would think, is due to a high anodic polarization. But this explanation is invalid because the activation potential of iron, ε_{ac}, is also close to +0.58 V, though in this case the iron electrode is polarized cathodically. In this connection it was assumed that, in spite of the fact that iron dissolves predominantly as bivalent ions, an oxide film may be formed with the participation of iron ions of a valency higher than 3. This is possible provided that iron is gradually oxidized by an excess of oxygen in the surface layer. Therefore, apart from the oxides FeO and Fe_2O_3, this oxide layer may also contain higher oxides, say FeO_2, which are characterized by more positive potentials. The passivation of nickel, for example, is explained analogously.

The existence of surface films of a phase nature has been proved experimentally by Kistyakovsky, Izgaryshev, Akimov and their colleagues. Evans (1930), who used specially selected solutions attacking only the metal and not the oxide film on its surface, succeeded in separating the film by carefully dissolving the underlying metal. Naturally, the continuity of the film had to be disturbed to a certain extent because otherwise the metal could not be dissolved. The data of electron-diffraction and optical investigations also confirm the existence of a film on the surface of a passive metal and, in a number of cases, permit one to identify its composition and structure.

According to the film theory, transpassivity is ascribed to the change of the composition and structure of a surface oxide due to the formation of higher-valency ions, which disturbs the continuity of the film. The protective action of the film is thus reduced and the metal can dissolve again, this time at more positive potentials and usually in the form of higher-valency ions. In the film theory, according to which passivity is caused by a surface oxide layer, much attention is paid to the formation and growth of this oxide layer. The main factors controlling this process are the potential of the metal and also the concentrations of metallic and hydroxyl ions. The potential of the metal must be sufficiently positive to provide the stability of the given oxide. The concentrations of metallic and hydroxyl ions must be sufficiently high for the corresponding principal salts or hydroxides to be formed. These compounds are then transformed to produce passivating oxides. Passivity will set in the more easily, the higher the electrode polarization in anodic metal dissolution and the lower the rate of removal of metallic ions from the electrode surface.

According to the adsorption theory, passivity is not necessarily connected with the formation of a polymolecular oxide film. It can be achieved through the retardation of the metal-dissolution reaction caused by adsorbed oxygen atoms. Oxygen atoms may appear on the metal surface from the discharge of hydroxyl ions (or water molecules)

at potentials lower than those at which oxygen is evolved or oxides are formed. The adsorbed oxygen atoms passivate the metal either by forming a continuous monomolecular layer on its surface or by blocking the most active centres, or else by changing the effective potential difference across the metal-solution interface. The suggestion that a continuous monomolecular layer of oxygen atoms is responsible for the passivation of a metal offers nothing radically new compared with the film theory, the more so that such a layer is scarcely distinguishable from a surface oxide. As regards the amount of oxygen, a monomolecular layer of its closely packed adsorbed atoms or molecules is equivalent to 2-4 molecular layers consisting of a surface oxide.

Of much greater interest is the possibility of passivation by blocking active centres on the surface of a dissolving metal or by retarding the dissolution process electrochemically. The surface of a dissolving metal being energetically nonuniform, the passage of its ions into solution from the various parts proceedsat different rates. If a certain number of oxygen atoms or molecules (too small to cover the entire surface) are adsorbed on sites where the metal is dissolved most easily, this will result in an abrupt fall in the overall rate of dissolution, entirely out of proportion with the surface covered with oxygen. This decrease of dissolution will increase polarization, i.e., will shift the anode potential to the positive side. This shift of potential will favour further oxygen adsorption and the attainment of the passive state. The next equal amount of oxygen will further decrease dissolution, though not so markedly as previously since this time less active centres are blocked, etc. If the difference in energy between the various parts of the surface is considerable, this mechanism of selective adsorption will decrease dissolution down to the value usually observed in the passivity region.

Still more effective is the adsorption-electrochemical mechanism of passivation (Ershler, Kabanov, Kolotyrkin, and others). The validity of this mechanism is confirmed, for example, by data on the dissolution of platinum. The rate of its dissolution in hydrochloric acid at a constant potential is exponentially dependent on the surface concentration of oxygen.

To provide a four-fold decrease of dissolution it is sufficient to deposit an amount of oxygen capable of covering about 4 per cent of the electrode's visible surface. The next equivalent amount of oxygen will lower the rate of dissolution by the same factor, i.e., the initial value will be reduced 16-fold; still another portion of oxygen will bring the figure down to 1/64th of the initial rate of dissolution, and so on until the dissolution of platinum stops. This exponential dependence is explained by Ershler as being due to the displacement from the double layer of an equivalent number

of anions by adsorbed oxygen atoms (which play the role of the negative end of the metal-oxygen dipole). The decrease in the number of anions in the double layer will accordingly lower the ionic potential difference, the total metal-solution potential difference remaining unchanged. According to the laws of electrochemical kinetics this must result in an exponential decrease of the rate of ionization, i.e., the rate of metal dissolution will drop down to the value observed experimentally.

The retardation of the dissolution process by the adsorption mechanism must be of special importance at the stage of transition from the active to the passive state.

Irrespective of which of these theories is considered more valid, the occurrence of passivation and the passive state proper must be related to the decrease of the rate of metal dissolution. It has therefore been suggested that passivity be defined as the state of the increased stability of a metal or alloy resulting from the hindered anodic process (Tomashov).

CHAPTER 24

Electrochemical Corrosion of Metals

24.1. GENERAL DESCRIPTION OF CORROSION PROCESSES

Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interaction with the environment. Corrosion is an undesirable and undeliberate process. The electrochemical dissolution of blister-copper anodes in copper-refining baths cannot be regarded as a corrosion process since it is a necessary and desirable link in the purification of copper. At the same time the electrochemical dissolution of an iron anode in a water-electrolysis bath should be included in the category of corrosion processes since it is undesirable in this case. The erosion of the walls of iron tanks in which sulphuric acid is transported is considered corrosive destruction, whereas the dissolution of iron in sulphuric acid for the purpose of producing pure reactive iron sulphate is not regarded as corrosion, though both processes are based on the same phenomena.

Corrosion is a spontaneous process occurring predominantly without application of an external current. This feature of corrosion is easy to understand considering that those metals (ferrous and nonferrous) are usually subject to corrosion which occur in nature as minerals or ores, and not in the native state. The winning of these metals from ores or minerals requires a certain amount of power. The same metals, when corroded, tend to revert to oxides, sulphides, carbonates and other compounds in which they occur under natural conditions. Since the corrosion process results in the recovery of the original compounds, which are thermodynamically more stable than the pure metals, it is accompanied by a decrease in free energy and therefore proceeds spontaneously. Metals that occur in a native state (e.g. gold, platinum) usually do not corrode under conditions which do not differ materially from those existing in nature. It is therefore not surprising that many metals are attacked rapidly, and losses due to corrosion sustained by all branches of the national economy are enormous. Five to twenty per cent of the ferrous metals produced annually are destroyed by corrosion. However great the direct loss due to corrosion, it cannot give an accurate idea of the actual damage caused by this process. Even a slight deterioration of a chemical apparatus by corrosion may put it out of service, upset and interrupt the technological process, lead to

wastage of time and materials, etc. The associated expenses are much higher than the cost of replacement material. For example, the relatively low cost of an underground lead cable length destroyed by corrosion stands no comparison with the expenses on the work required to locate the damage, remove the ground and repair the cable.

24.2. CLASSIFICATION OF CORROSION PROCESSES

A distinction is made between chemical, biochemical and electrochemical corrosion of metals.

Chemical corrosion of metals is spontaneous destruction governed by the laws of ordinary heterogeneous chemical reactions. The destruction of metals attacked at high temperatures by aggressive gases which prevent condensation of moisture on the metal surface, and also, evidently, the dissolution of metals in contact with non conducting organic media belong to the category of chemical corrosion processes.

Biochemical corrosion, or biocorrosion, is caused by the vital activity of various microorganisms using a metal as a culture medium or evolving products which attack the metal. Biochemical corrosion usually accompanies other types of corrosion. Soils of definite composition, stagnant waters and certain organic products greatly favour the progress of biochemical corrosion.

Electrochemical corrosion is encountered more frequently than other types of corrosive destruction and is most dangerous to metals. It may occur in a gas atmosphere, when moisture condenses on the metal surface (atmospheric corrosion), in soils (soil corrosion) and in solutions (liquid corrosion). Electrochemical corrosion is governed by the kinetics of electrochemical reactions. Its rate can be determined on the basis of Faraday's law.

A special case of electrochemical corrosion is electrocorrosion, i.e., corrosion caused by an external electric current. Apart from the destruction of insoluble anodes, electrocorrosion includes the corrosion of pipelines with current-conducting liquids flowing through them and also the dissolution of the walls of electrolytic baths and underground metal structures under the influence of a direct current from bare electric lines (stray-current corrosion). The stray currents may set up a potential difference between two portions of a metal structure, one receiving current from some external source of electrical energy (cathodic area) and the other acting as the anode (anodic area), from which the current flows into the surrounding ionically conducting medium, the anodic portion being destroyed.

According to the mode of destruction accompanying electrochemical corrosion, a distinction is made between general corrosion,

affecting the entire surface of a metal, and local corrosion, confined to definite parts of the metal surface. In the latter case corrosion may result in stains (stain corrosion) or pits (pitting). This corrosion may involve grains of a single component of a metal alloy (selective corrosion), penetrate all grains, thereby forming narrow cracks (transcrystalline corrosion) or, finally, concentrate along grain boundaries (intergranular or intercrystalline corrosion). The rate and nature of electrochemical corrosion are largely determined by the nature of the metal and its environment. According to the rate of corrosion in a particular medium metals are classified as stable and unstable. Based on the rate with which a given medium corrodes the metal, it is defined either as aggressive or nonaggressive. Various conventional scales have been suggested to estimate the corrosion resistance of metals and the aggressiveness of media. The rate of corrosion is expressed in several ways. The weight and current indices are used most frequently. The first shows the weight loss (in grams or kilograms) per unit time (second, hour, day, year) referred to a unit area (square centimetre, square metre) of a test specimen. In the second case the corrosion rate is given in terms of current intensity (in amperes or milliamperes) per unit surface area of the specimen.

24.3. CONDITIONS FOR THE OCCURRENCE OF A CORROSION PROCESS

The corrosion of metals is a special case of nonequilibrium electrode processes; at the same time it has its own specific features distinguishing it from other irreversible electrode processes. The application of an external current is not a necessary precondition for a corrosion process and nevertheless the dissolution of a metal under corrosion conditions proceeds at rates comparable to those observed in the dissolution of metallic anodes in industrial electrolyzers. For example, in zinc-plating processes the anodic current density ranges from 50 to 500 A/m^2, depending on the composition of the electrolyte used, and the rate of corrosion of technical zinc in $1N$ H_2SO_4 is equivalent to a current density of 100 A/m^2, i.e., is of the same order of magnitude. The factors responsible for such high rates of metal dissolution in the absence of an external anodic current are hidden in the specificity of the corrosion process.

Suppose that a piece of a metal M is brought into contact with an aqueous solution of its salt MA; after some time a potential will be set up at the metal-solution interface, which will then remain practically unchanged. This constant (or almost constant) value corresponds either to an equilibrium between the metal and the solution or to steady-state conditions of an electrode process. Which of these cases is actually realized is determined primarily

by the magnitude of the electrode potential. If the thermodynamic electrode potential of the metal has a value at which, under the given conditions, all processes, other than the exchange of metallic ions between the metal and the solution, are excluded, the final value of the potential will correspond to its equilibrium value under the given conditions. Under equilibrium conditions the rate of ion transfer in two opposite directions will be the same and equal to the exchange current:

$$\vec{I}_M = \overleftarrow{I}_M = I_M^0$$

and the potential attained will correspond to the thermodynamic value. An example of such a system is silver immersed in a solution of silver nitrate.

The situation is changed substantially if the thermodynamic electrode potential of the metal has a value at which, apart from the ionization and the discharge of metallic ions, at least one additional electrode process is possible. In this case, charges are transferred across the metal-solution interface by two species of particles instead of one. The constant potential does not necessarily imply here the attainment of the equilibrium state. It only indicates that the total number of charges crossing the interface in one direction is equal to the total number of charges crossing it in the opposite direction, i.e., that

$$\vec{i} = \overleftarrow{i} \tag{24.1}$$

If it is assumed that the additional electrode process is the evolution and ionization of hydrogen, so-called corrosion with hydrogen depolarization, then one can write in place of Eq. (24.1):

$$\vec{i}_M + \vec{i}_H = \overleftarrow{i}_M + \overleftarrow{i}_H \tag{24.2}$$

where M refers to a metal and H to hydrogen. If the rates of all partial processes are comparable and none of these rates can be ignored in Eq. (24.2), the steady-state mixed potential will correspond neither to the potential of a metal electrode of the first kind (or a metal electrode of the second kind, if the metal is covered with a layer of its sparingly soluble compound) nor to the hydrogen electrode potential. It will be a certain mixed potential dependent on the ratio of the rates of all the partial reactions (Fig. 24.1). It may happen, however, that the potential of a given electrode does not differ markedly from either the hydrogen electrode potential or the potential of a corresponding metal electrode. Indeed, though the partial currents in Eq. (24.2) do not correspond to the exchange currents under equilibrium conditions, they must still vary together with exchange currents. Therefore, if the exchange current of the metal, i_M^0, is much higher than that of hydrogen, i_H^0, it may be

assumed, to a certain approximation, that

$$\vec{i}_M \gg \vec{i}_H$$

and

$$\overleftarrow{i}_H \gg \overleftarrow{i}_H$$

Then, in place of Eq. (24.2) one can write

$$\vec{i}_M \approx \overleftarrow{i}_M$$

Hence, the behaviour of a corroding electrode corresponds to that of a reversible metal electrode, and the steady-state mixed potential is close to the equilibrium potential of a corresponding metal

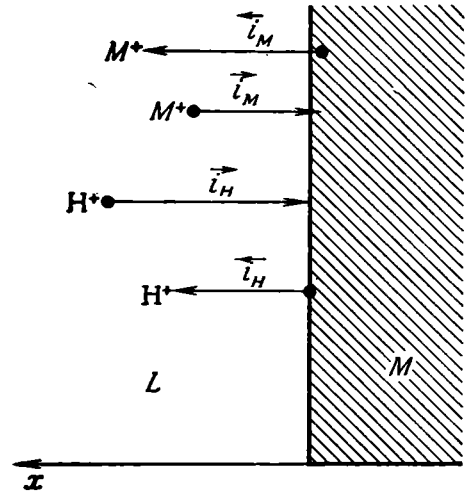


Fig. 24.1. Scheme for the mixed (or stationary) corrosion potential ε_{cor} being attained at comparable rates of the anodic and cathodic reactions: $\vec{i}_M + \vec{i}_H = \overleftarrow{i}_M + \overleftarrow{i}_H$; $\varepsilon_{cor} \neq {}_M\varepsilon_r$; $\varepsilon_{cor} \neq {}_H\varepsilon_r$

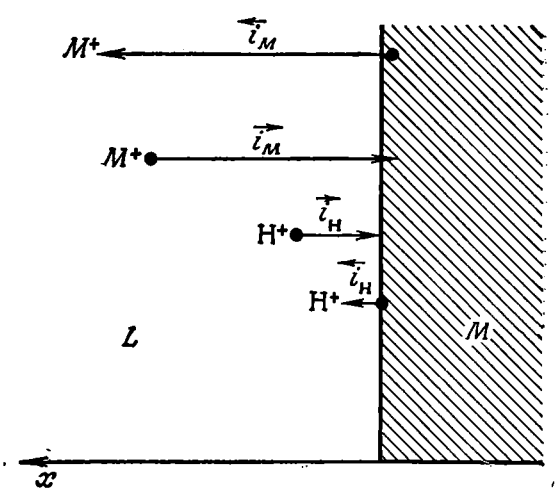


Fig. 24.2. Scheme for the mixed (or stationary) corrosion potential ε_{cor} being attained when the exchange current for a metal is higher than that for hydrogen: $i^0_M \geqslant i^0_H$; $\vec{i}_M = \overleftarrow{i}_M$; $\varepsilon_{cor} \approx {}_M\varepsilon_r$

electrode (Fig. 24.2) and must vary with the concentration of metallic ions according to Nernst's formula. The variation of the solution pH does not here affect markedly the stationary potential. Thus, the stationary corrosion potential ε_{cor} is reduced here to the reversible potential of the metal, ${}_M\varepsilon_r$, i.e.,

$$\varepsilon_{cor} \approx {}_H\varepsilon_r$$

Examples of such systems are the decomposition of amalgams and the electrochemical dissolution of zinc.

Conversely, if the exchange current of hydrogen is much higher than that of the metal, then

$$\vec{i}_M \ll \vec{i}_H$$

and

$$\overleftarrow{i}_M \ll \overleftarrow{i}_H$$

and, to a certain approximation,

$$\overrightarrow{i}_H \approx \overleftarrow{i}_H$$

In this case the mixed potential is close to the hydrogen electrode potential under the given conditions (Fig. 24.3). Its value varies regularly with pH of the solution and is almost independent of the concentration of metallic ions. Thus, here the stationary potential is reduced to the hydrogen electrode potential, i.e.,

$$\varepsilon_{cor} \approx {}_H\varepsilon_r$$

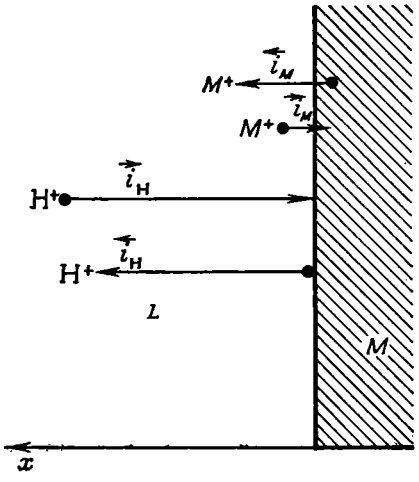


Fig. 24.3. Scheme for the mixed (stationary) corrosion potential ε_{cor} being attained when the exchange current for a metal is lower than that for hydrogen: $i^0_M \gg i^0_H$; $\overrightarrow{i}_H \simeq \overleftarrow{i}_H$; $\varepsilon_{cor} \approx {}_H\varepsilon_r$

The corrosion of iron in weakly acidic solutions is an example.

The necessary condition for electrochemical corrosion is the simultaneous occurrence, on the surface of a corroding metal, of ionization and discharge of its ions and any other electrode reaction proceeding predominantly in the cathodic direction. In aqueous media containing no oxidants other than hydrogen ions and dissolved oxygen, this condition is met only if the equilibrium potential of the metal is more negative than the equilibrium potential of the hydrogen or oxygen electrode in a solution of a given composition. The introduction into the solution of other oxidants with a more positive equilibrium potential increases the number of corrodible metals[1]. For example, silver, which is stable in aqueous solutions of nonreducible acids, corrodes on addition of an oxidant with a potential more positive than the equilibrium potential of a silver electrode.

24.4. THE KINETIC THEORY OF CORROSION AND ITS APPLICATION TO PURE METALS

The possibility of the dissolution of a metal indicates that under given conditions the rate of ionization is higher than the rate of

[1] Though the presence of a stronger oxidant in the solution increases the thermodynamic probability of corrosion, it does not necessarily increase its rate.

discharge of its ions

$$\vec{i}_M < \overleftarrow{i}_M$$

In the absence of externally applied current and with the potential remaining unchanged this ratio of the rates is possible if the rate of discharge of hydrogen ions exceeds the rate of the reverse process by the same amount, i.e.,

$$\vec{i}_H > \overleftarrow{i}_H$$

The corrosion rate i_{cor} may be represented as the difference between the rate of ionization and the rate of discharge of metallic ions

$$i_{cor} = \overleftarrow{i}_M - \vec{i}_M \tag{24.3}$$

Since Eq. (24.2) is valid for the corrosion process, one can also write in place of (24.3)

$$i_{cor} = \vec{i}_H - \overleftarrow{i}_H \tag{24.4}$$

and define the corrosion rate as the difference between the rate of discharge of hydrogen ions and that of ionization of hydrogen molecules. This permits calculating the rate of corrosive destruction of a metal from data on the kinetics of the evolution and ionization of hydrogen in corrosive conditions.

The application of these principles to the calculation of the rate of self-dissolution of metals may be illustrated by the corrosion of zinc and iron in a solution of pH = 0 and unit activities of the corresponding metallic ions. Under the conditions chosen the potential of zinc (assuming that only the exchange of its ions between metal and solution is taking place) must correspond to its standard potential, i.e., —0.76V. At this potential, however, the exchange of zinc ions is not the only possible process. The value of this potential is considerably more negative than the potential of the equilibrium hydrogen electrode, which is ±0.0V in a solution of pH = 0. Therefore in this case the evolution of hydrogen is also possible, proceeding at a rate determined by the kinetics of this reaction on a zinc electrode.

The steady-state value of the potential will be intermediate between the zinc potential and the hydrogen potential, i.e., it must lie somewhere between zero and —0.76V on the hydrogen scale. Its actual position between these two values depends on the exchange currents of the competing reactions. The exchange current on zinc is about 10^{-5} A/cm^2, and that on a zinc electrode, about 10^{-10} A/cm^2. From this ratio of exchange currents it follows that the stationary potential of the zinc electrode under the conditions in question may be reduced to its equilibrium potential, i.e., it must

not differ markedly from —0.76V. At the same time the steady-state potential is shifted far to the negative side from the potential of the reversible hydrogen electrode. It will correspond to the hydrogen overpotential, which is close to —0.76V, since

$$\eta_H = \varepsilon_i - {}_H\varepsilon_r = -0.76 - 0.00 = -0.76V$$

At this deviation from equilibrium the rate of hydrogen ionization may be ignored, in which case Eqs. (24.3) and (24.4) may be rewritten in the form

$$i_{cor} = \overleftarrow{i}_M - \overrightarrow{i}_M = \overrightarrow{i}_H \tag{24.5}$$

Knowing the stationary potential and the corresponding hydrogen overpotential, one can easily calculate the rate of hydrogen evolution $\overrightarrow{i}_H$ and, hence, the metal corrosion rate i_{cor}. In the case under consideration both the stationary potential of zinc, ${}_{Zn}\varepsilon_{cor}$, and the hydrogen overpotential ${}_{Zn}\eta_H$ are equal to —0.76V. Substituting into Tafel's formula

$$\eta = a + b \log i$$

the values of a and b (see Table 19.1, page 415) for hydrogen evolution at zinc from acidic solutions (at pH = 0) and the value of hydrogen overpotential at the stationary corrosion potential, one has

$$-0.76 = -1.24 - 0.12 \log \overrightarrow{i}_H$$

whence

$$\overrightarrow{i}_H = 10^{-\frac{1.24-0.76}{0.12}} = 10^{-4} A/cm^2$$

Thus, the rate of corrosion of pure zinc under the chosen condition is 10^{-4} A/cm^2 or 1 A/m^2. This value is in good agreement with experimental data on the corrosion of pure zinc. At the same time it is considerably lower than the rate of corrosion of technical zinc.

In the case of iron the standard electrode potential is —0.44V. Therefore, as with zinc, one should reckon with hydrogen evolution and, hence, the steady-state conditions will be given by Eq. (24.2). But, in contrast to zinc, the ratio of exchange currents here is entirely different. The exchange current of iron is of the order of 10^{-9} A/cm^2, and for hydrogen on an iron electrode in acid solutions it reaches 10^{-6} A/cm^2. It can therefore be expected that the stationary potential of iron under the conditions of acidic corrosion must differ markedly from its reversible potential; it will be shifted to the side of negative values, i.e., in the direction of the equilibrium potential of the hydrogen electrode. This conclusion agrees with experimental evidence and is additionally confirmed by the fact that iron behaves like a hydrogen electrode within certain ranges of pH values.

The rate of iron corrosion can also be calculated provided its stationary potential and the overpotential at which hydrogen is evolved on it are known.

The phenomena of electrochemical corrosion were first kinetically interpreted by Frumkin (1932), who noted that the decomposition of alkali-metal amalgams obeys the laws of electrochemical kinetics. This idea was treated quantitatively by Wagner and Traud (1938), who succeeded in obtaining good agreement between theory and experimental data on the rates of decomposition of zinc amalgams. Similar views were expressed by Shultin, Durdin, and a number of other authors. The usefulness of the laws of electrode kinetics for quantitative description of the corrosion of solid metals was proved by Kolotyrkin and also by Scorcelletti, Grin, and others. The works of these scientists have exerted a considerable influence on the formulation of modern concepts of corrosion processes and contributed to the establishment of a link between electrochemical science and the theory of metal corrosion. The kinetic theory of corrosion is often called incorrectly the "homogeneous-electrochemical theory" or "homogeneous-electrochemical mechanism" of corrosion. The term "homogeneous" should not be applied to the corrosion process, which always takes place at the interface between two phases at least and is therefore a typical heterogeneous process by its nature. It would be more correct to call it the kinetic theory.

24.5. CORROSION OF TECHNICAL METALS

All the considerations expressed above concerning the corrosion process and the calculations based on them referred to the electrochemical dissolution of a pure metal with a surface completely homogeneous in its properties. In practical situations, it is technical metals that are usually subject to corrosion, i.e., metals containing impurities of other metals and nonmetallic substances. Inclusions of foreign metals can always be detected on the surface of these metals. Besides, the surface of technical metals is usually covered with products of their interaction with the environment, various contaminations, etc. Naturally, the heterogeneity of a metal surface and, primarily, the presence on it of foreign metals having different electrochemical properties must affect the rate of corrosion and its mode of occurrence. Technical zinc, for example, usually contains lead, silver, and iron impurities. As follows from the values of standard potentials, all these metals are more electropositive than zinc. It may therefore be supposed that zinc alone is undergoing corrosion, while the impurities remain intact. This assumption agrees with experimental data. Suppose that in each of these cases an impurity metal is present in such an amount that it occupies 1 per cent of the entire surface of a zinc specimen in contact with an acid solution.

If the conditions are the same as in the case of pure zinc (pH = 0 and $a_{Zn^{2+}} = 1$), the corrosion of zinc must involve hydrogen depolarization and its rate is determined by the kinetics of hydrogen evolution on the corroding metal. In contrast to ultrapure zinc, in this case hydrogen can be discharged not only on zinc but also on an impurity metal. The overall rate of hydrogen evolution and, hence, the overall rate of zinc dissolution are therefore determined by the kinetics of hydrogen evolution at the principal metal and at impurity inclusions. Using the data of Table 19.1 and substituting them into Tafel's formula, we can write the following equations for the overpotentials at which hydrogen is evolved at the principal metal[1] and at its impurity inclusions:

$$_{Zn}\eta_H = -1.24 - 0.12 \log {}_{Zn}i_H \tag{24.6}$$

$$_{Pb}\eta_H = -1.56 - 0.12 \log {}_{Pb}i_H \tag{24.7}$$

$$_{Ag}\eta_H = -0.95 - 0.12 \log {}_{Ag}i_H \tag{24.8}$$

and

$$_{Fe}\eta_H = -0.70 - 0.12 \log {}_{Fe}i_H \tag{24.9}$$

where $_{M}i_H$ is the rate of hydrogen evolution on a given metal at the overpotential $_{M}\eta_H$; for ultrapure zinc it is denoted by $_{Zn}i_H$. Hydrogen evolves at this rate on 99 per cent of the surface of the metal, namely, on zinc. On the remaining part of the surface (1 per cent) occupied by an impurity the evolution of hydrogen proceeds at the rate $_{M}i_H$ determined by the hydrogen overpotential on a given metal. Hence, the overall rate of hydrogen evolution on the entire surface of the technical metal may be written as

$$i_{cor} = \vec{i}_H = 0.99 \, {}_{Zn}i_H + 0.01 \, {}_{M}i_H \tag{24.10}$$

Suppose the surface of a technical metal is equipotential under corrosion conditions; the quantity $_{M}i_H$ for any impurity metal can then be expressed in terms of the rate of hydrogen evolution at zinc, $_{Zn}i_H$. For example, from Eqs. (24.6) and (24.7) it follows that in the case of lead inclusions

$$_{Pb}\eta_H = {}_{Zn}\eta_H = {}_{Zn}\varepsilon_{cor} - {}_{H}\varepsilon_r$$

or

$$-1.24 - 0.12 \log {}_{Zn}i_H = -1.56 - 0.12 \log {}_{Pb}i_H$$

from which

$$\frac{{}_{Pb}i_H}{{}_{Zn}i_H} = 10^{-\frac{1.56-1.24}{0.12}} = 10^{-2.7} \tag{24.11}$$

---

[1] The values of Tafel constant b for all metals are rounded to 0.12.

Substituting the value of ${}_{Pb}i_H$ into Eq. (24.10) for ${}_{M}i_H$, one obtains

$$i_{cor} = \vec{i}_H = 0.99\ {}_{Zn}i_H + 0.01 \times 10^{-2.7}\ {}_{Zn}i_H = \\ = (0.99 + 0.00002)\ {}_{Zn}i_H \approx 0.99_{Zn}i_H \qquad (24.12)$$

Thus, the presence in zinc of impurities of lead, a metal with the higher overpotential, does not increase the rate of corrosion but reduces it somewhat. Different ratios result if silver is present as an impurity. In this case the rate of hydrogen evolution at one and the same value of overpotential is higher on silver than on zinc, and the ratio of the rates is

$$\frac{{}_{Ag}i_H}{{}_{Zn}i_H} = 10^{2.4}$$

Using this ratio, one can easily determine the change of the corrosion rate in going from ultrapure zinc to technical zinc containing 1 per cent of silver

$$i_{cor} = \vec{i}_H = 0.99\ {}_{Zn}i_H + 0.01 \times 10^{2.4}\ {}_{Zn}i_H = \\ = (0.99 + 2.5)_{Zn}i_H \approx 3.5_{Zn}i_H \qquad (24.13)$$

Hence, the presence of silver in zinc must increase its rate of corrosion. Under the conditions chosen this rate increases by a factor of 3.5. The increase of the rate of dissolution however is not the only result of contamination of zinc with silver. The nature of corrosion also changes. Indeed, whereas in the previous case all hydrogen evolved on the zinc surface, i.e., on the same surface where the dissolution (ionization) of zinc took place, here, as can easily be determined with the aid of Eq. (24.13), only 26 per cent of hydrogen is evolved on zinc, the remaining 74 per cent being evolved on silver. Silver will not dissolve since it has an electropositive potential; only the cathodic process—hydrogen evolution—is possible on it. When containing inclusions of silver, zinc behaves as an anode and is the scene of the whole process of dissolution. Besides, zinc also plays the role of a cathode, providing the evolution of one-fourth of the total amount of discharging hydrogen.

A still higher increase of the corrosion rate and a more complete separation of the metal surface into the anodic and cathodic parts should be expected when zinc is contaminated with iron. In this case

$$i_{cor} = \vec{i}_H = 0.99\ {}_{Zn}i_H + 0.01 \times 10^{4.5}\ {}_{Zn}i_H = \\ = (0.99 + 531)\ {}_{Zn}i_H \approx 352_{Zn}i_H \qquad (24.14)$$

and the corrosion rate must increase by 350 times[1]. The amount

[1] The actual increase of the corrosion rate will not be so high since iron forms with zinc intermetallic compounds on which the overpotential is higher than on iron.

of hydrogen evolved on the iron surface is 99.8 per cent, and only 0.02 per cent is evolved on zinc. In this case the anodic and cathodic reactions are spatially separated. The anodic reaction is confined to the zinc surface, and the cathodic one, to the surface of iron inclusions.

Under these conditions the corroding zinc is an assembly of galvanic microcells in each of which the iron is the positive pole and

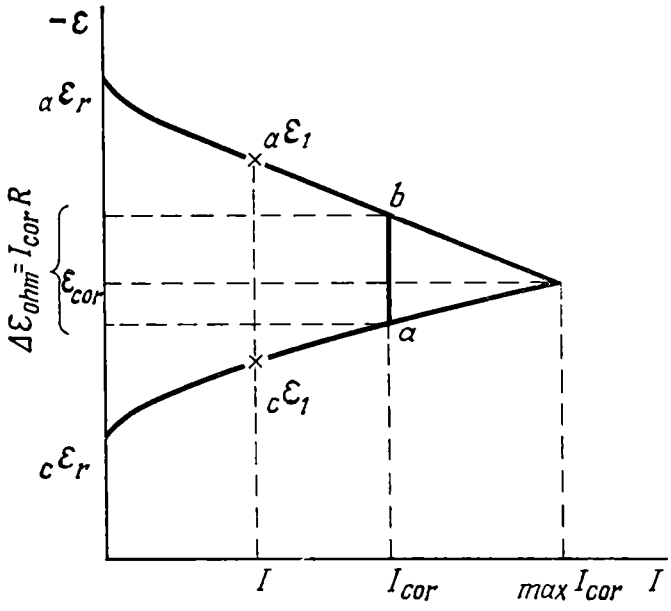


Fig. 24.4. Corrosion diagram (potential-current curve)

the anodically dissolving zinc, the negative one. On this basis the corrosion of a metal with inclusions of other metals is the result of the operation of local cells.

This concept of metal corrosion was advanced more than 100 years ago by de la Rive on the basis of observations of hydrogen evolution in the dissolution of zinc in an acid. Later, owing to the works of many scientists (Sluginov, Evans, Hoar, Mears, Palmaer, Akimov, Tomashov, and others), these views were developed into the first electrochemical theory of corrosion, the so-called local-cell theory of corrosion.

According to the local-cell theory of corrosion the corrosion rate (or the corresponding electric current produced by local voltaic couples) depends not only on the electrochemical properties of the electrodes of these couples but also on the ohmic resistance of the medium in which the corrosion process occurs and which separates the anode from the cathode. The relation for the corrosion rate can be conveniently expressed with the aid of so-called corrosion diagrams (Evans diagrams). Figure 24.4 shows a corrosion diagram

where the anode and cathode potentials or the potentials of the anodic and cathodic processes are given as a function of the current. When there is no corrosion and the current is equal to zero, the initial values of the anode and cathode potentials must correspond to the reversible potentials of the anodic ($_a\varepsilon_r$) and cathodic ($_c\varepsilon_r$) reactions under given conditions. The potential difference between the anode and cathode potentials gives rise to a current in the system. At a current I the anode potential is shifted, due to polarization, to more positive, and the cathode potential to more negative values. Let these quantities be equal to $_a\varepsilon_1$ and $_c\varepsilon_1$, respectively. The difference between these potentials with a current flowing is smaller than that between the reversible potentials. With increasing current the difference between the anode and cathode potentials decreases continuously. In the limit it is equal to zero and the surface of the corroding metal is equipotential. The current now corresponds to the maximum possible rate of corrosion $_{max}I_{cor}$ under the given conditions and the potential of the metal becomes equal to ε_{cor}, which lies between $_a\varepsilon_r$ and $_c\varepsilon_r$. This maximum current can be attained provided only that the resistance of the system is either zero or negligibly small. But if the ohmic potential drop is not zero, the corrosion rate will be equal to I_{cor}, which is smaller than $_{max}I_{cor}$. Under these conditions the ohmic potential drop $\Delta\varepsilon_{ohm}$ is numerically equal to the length of section ab. During the corrosion process the anode potential will be $\Delta\varepsilon_{ohm}$ more negative than the cathode potential. Thus, the corrosion rate is a function of the difference between the reversible potentials of the anodic and cathodic reactions, electrode polarizability and the ohmic resistance of the corrosive medium. The effect of each of these factors on the corrosion rate is represented graphically in Fig. 24.5 in the form of simplified corrosion diagrams. The corrosion rate decreases if the reversible potentials of the anodic and cathodic reactions become close to each other at a given resistance and constant polarizability of the electrodes (Fig. 24.5*a*), i.e., I_{cor} varies along with the quantity $(_c\varepsilon_r - {}_a\varepsilon_r)$. The corrosion rate decreases with increasing total resistance in the system corroding metal/corrosive medium (Fig. 24.5*b*). It also diminishes as the anodic or cathodic polarization increases (Fig. 24.5 *c* and *d*, respectively). Polarization increases when the anodic and cathodic reactions are additionally hindered or when the anodic and cathodic areas become smaller. When the surface area of a given electrode is reduced at a constant current, the current density at this electrode increases and so does its polarization.

In the local-cell theory it was originally assumed that the cathodic and anodic processes are spatially separated and each of these reactions proceeds only on a definite part of the corroding metal surface. It was concluded on this basis that ideally pure metals with a highly homogeneous surface are not subject to corrosion. This conclu-

sion however is erroneous both from the thermodynamic and kinetic points of view. A necessary precondition for corrosion is a difference between the reversible potential of the metal and the potentials of the anodic and cathodic reactions possible under given conditions and not the spatial separation of cathodic and anodic areas. Depending on the extent of homogeneity of the metal-medium interface, the anodic and cathodic reactions may proceed on one

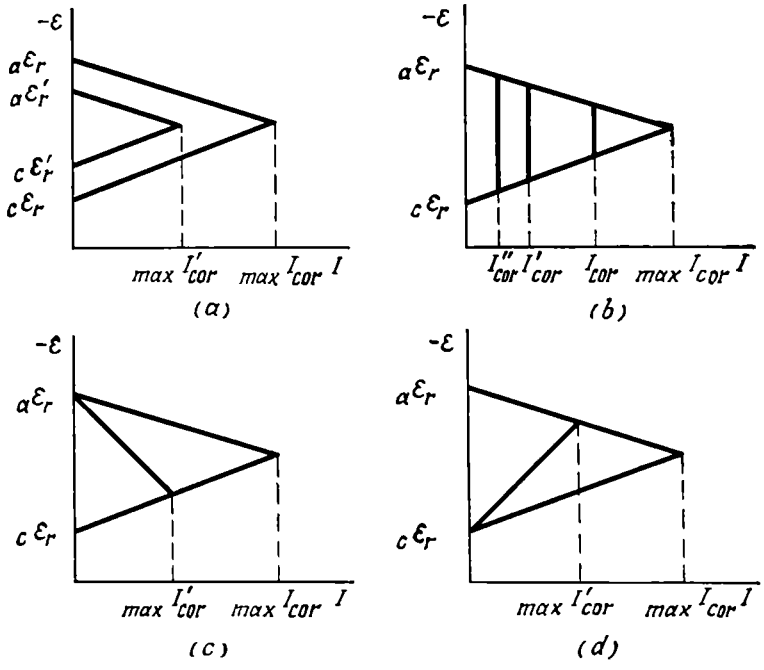


Fig. 24.5. Corrosion diagrams illustrating the effect of various factors on the corrosion rate

and the same surface or on its different areas. The simultaneous occurrence of cathodic and anodic reactions during corrosion is typical of pure metals and amalgams; a more or less complete spatial separation of these reactions is characteristic of the corrosion of technical metals. The low stability of technical metals as compared with pure metals and also the change of the mode of corrosion are largely associated with the operation of galvanic microcells basis metal-inclusion.

Corrosion diagrams (potential-current curves) constructed on the basis of the local-cell theory are convenient for qualitative treatment of the corrosion process and for estimation of the possible effects of various factors on this process. At the same time the use of these diagrams in quantitative calculations of the corrosion rate entails considerable difficulties. The corrosion rate is determined by the

change in the weight of a metal specimen per unit time referred to unit area of its surface or (in electrical units) by the current density i_{cor}. The corrosion diagrams presented in Figs. 24.4 and 24.5 are plotted in the potential-current coordinates, i.e., they do not include the current density, which is a direct characteristic of the corrosion rate. Additional data are therefore needed to calculate the current density. It is necessary to know the qualitative composition of a corroding metal in order to find out which components of the metal will act as the cathode and which as the anode. One has to find out the fraction of the surface represented by each cathodic and anodic area in order to determine the current density on any of these areas. Further, anodic polarization curves must be traced for all the anodic components and cathodic polarization curves for all the cathodic components. All this allows one to find the overall rate of the cathodic and anodic reactions and to identify the most effective anodic and cathodic components. Knowing the stationary potentials, one can, by summing up all the cathodic and anodic curves, plot a net corrosion diagram and use it to determine the maximum possible current. Assuming the ohmic potential drop to be small and knowing the proportion between the anodic and cathodic areas, one can calculate the rate of corrosion. This complicated method, which does not always yield unambiguous data (because cathodic and anodic reactions may occur simultaneously on one and the same surface area) is rarely used for quantitative estimation of the corrosion rate.

The rate of corrosion can be more conveniently determined with the aid of the kinetic theory of corrosion. In this case cathodic and anodic polarization curves are traced directly on the metal whose corrosion is studied. The overall rate of corrosion is expressed in terms of the current referred to unit area of the entire metal surface without separating it into anodic and cathodic areas. At the stationary potential the corrosion rate expressed in terms of the metal-dissolution current referred to the entire surface area (i.e., including cathodic areas) must be equal to the rate of the cathodic process, e.g. hydrogen evolution. If the cathodic polarization curve is traced, the rate of the cathodic reaction will be equal to the current divided by the total surface area of the test specimen, including the anodic areas. Thus, if the potential is stationary, the current densities for the anodic and cathodic processes must be equal if polarization curves are traced by the method indicated.[1] The ohmic potential drop is ignored here and hence the surface of the corroding

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[1] The actual cathodic and anodic current densities may be different if the surface of the corroding metal has areas on which either only a cathodic or only an anodic reaction may occur. This is not essential however when determining the overall rate of corrosion.

metal is assumed to be equipotential.[1] The form of combined polarization curves obtained by this method is shown in Fig. 24.6 (solid lines). The point of intersection of the anodic and cathodic polarization curves yields the corrosion rate on the abscissa, and the stationary potential on the ordinate. Since near the stationary potential the polarization data cease to fall within a semilogarithmic plot, the corrosion rate is found from the point of intersection of the

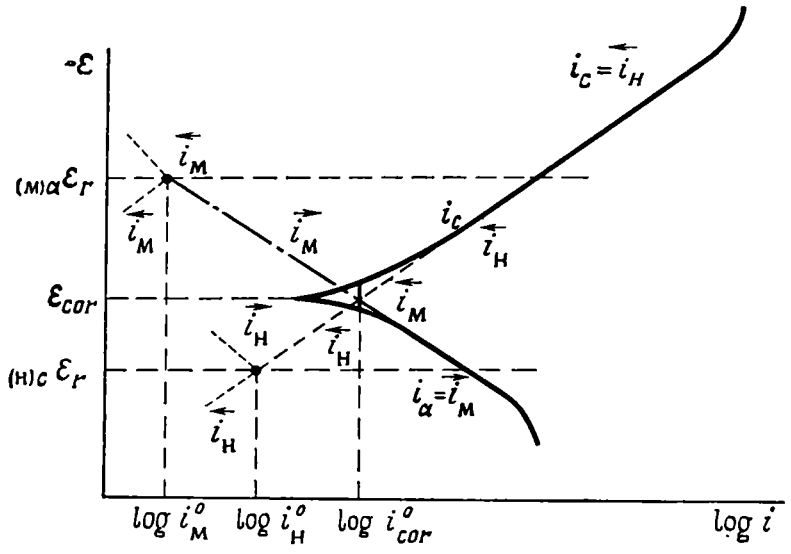

Fig. 24.6. Polarization diagram for corrosion with hydrogen depolarization. The solid lines are combined polarization curves, and the dot-and-dash lines are extrapolated curves

extrapolated straight-line portions of the polarization curves (see dashed lines in Fig. 24.6). A comparison of corrosion rates calculated on the basis of polarization measurements with those obtained directly from the weight loss (or from the volume of hydrogen evolved in acid media) for lead, nickel and iron has shown that both rows of data coincide within experimental error. That is why the method of polarization measurements is widely used in quantitative studies of corrosion processes.

The stationary corrosion potential ε_{cor} lies, as a rule, between the reversible potentials of the anodic and cathodic processes causing corrosion. It is always more positive than the equilibrium potential of the anodic reaction and more negative than the potential of the cathodic reaction. Therefore, at the corrosion potential the rate of ionization $\overleftarrow{i}_M$ of a metal is higher than the rate of discharge of

[1] The validity of this assumption for most processes of electrochemical corrosion follows from the experimental data obtained by Tomashov and Akimov together with Golubev and also from the theoretical calculations carried out by Frumkin and Levich.

metallic ions $\vec{i}_M$, and the rate of discharge of hydrogen ions $\vec{i}_H$ is higher than the rate of ionization of its molecules $\overleftarrow{i}_H$. These ratios persist until the corresponding equilibrium potentials are attained. In this case the partial currents for each of the two processes will become equal to the corresponding exchange currents i^0_M and i^0_H. The continuation of the cathodic and anodic polarization curves from the stationary potential to the reversible potentials of the electrode reactions is shown in Fig. 24.6 by dot-and-dash lines. The rate of corrosion is a function of the exchange current of the cathodic and anodic reactions. It rises with increasing exchange current (at the same equilibrium potentials). The corrosion rate must vary along with the transfer coefficient α. Thus, corrosion diagrams enable one to relate the rate of corrosion to the kinetic parameters controlling its basic electrode reactions. This relation can also be expressed analytically. At the stationary potential the corrosion rate must be equal to the rate of metal dissolution and also to the rate of the cathodic reaction (in the case under consideration, to the rate of the cathodic hydrogen evolution). On this basis one can write the following equation

$$i_{cor} = i^0_H e^{-\frac{\alpha F}{RT} {}_H\eta_c} = i^0_M e^{\frac{(1-\alpha'_2)zF}{RT} {}_M\eta_a} \tag{24.15}$$

where ${}_H\eta_c$ and ${}_M\eta_a$ = cathodic polarization for hydrogen evolution and anodic polarization for metal dissolution, respectively

α and α'_2 = transfer coefficients for hydrogen evolution and metal dissolution, respectively

z = valency of the metal.

During corrosion the hydrogen overpotential is equal to the difference between the corrosion potential and the reversible potential of the hydrogen electrode under the given conditions:

$$\eta = \varepsilon_{cor} - {}_H\varepsilon_r \tag{24.16}$$

An analogous equation is valid for the anodic polarization of the metal:

$$\eta_M = \varepsilon_{cor} - {}_M\varepsilon_r \tag{24.17}$$

Solving Eqs. (24.15), (24.16) and (24.17) simultaneously yields the following expression for the stationary corrosion potential ε_{cor}:

$$\varepsilon_{cor} = 2.303 \frac{RT}{(\alpha_1 + \alpha_2 z) F} \log \frac{i^0_H}{i^0_M} + \frac{\alpha_1}{\alpha_1 + \alpha_2 z} {}_H\varepsilon_r + \frac{\alpha_2 z}{\alpha_1 + \alpha_2 z} {}_M\varepsilon_r \tag{24.18}$$

Substituting this value of ε_{cor} into Eq. (24.15) leads, after some transformations, to the equation

$$\log i_{cor} = \log (i_M^0)^{\frac{\alpha_1}{\alpha_1+\alpha_2 z}} (i_H^0)^{\frac{\alpha_2 z}{\alpha_1+\alpha_2 z}} + \frac{\alpha_1 \alpha_2 z F}{2.303 (\alpha_1+\alpha_2 z) RT} ({}_H\varepsilon_r - {}_M\varepsilon_r) \tag{24.19}$$

In Eqs. (24.18) and (24.19), for simplicity, the subscripts a and H in ${}_a\eta_M$ and η_H are omitted and the quantity $(1 - \alpha_2')$ is denoted as α_2. Equations (24.18) and (24.19) are valid if the equilibrium

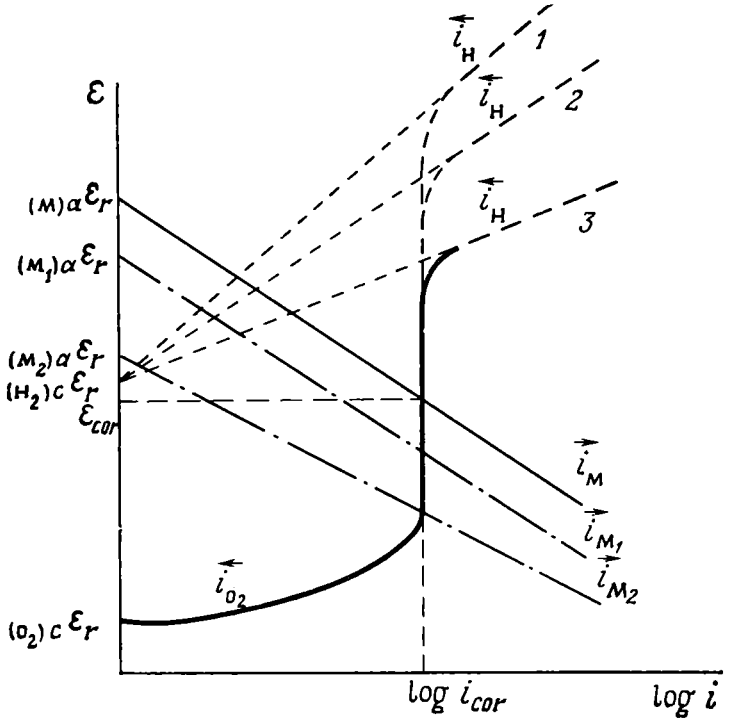

Fig. 24.7. Simplified polarization diagram for corrosion with oxygen depolarization

potential of the metal ${}_M\varepsilon_r$ is more negative than the hydrogen equilibrium potential ${}_H\varepsilon_r$. Equations (24.18) and (24.19) permit calculating the potential of a metal undergoing corrosion and also the rate of corrosive destruction provided only that the exchange currents, transfer coefficients and the equilibrium potentials of the anodic and cathodic reactions are known.

The polarization diagram in Fig. 24.6 and also Eqs. (24.18) and (24.19) refer to the case where the corrosion rate is determined by purely kinetic limitations, i.e., by activation polarization. This corresponds to corrosion with hydrogen depolarization. Another important case of electrochemical destruction of metals is their

corrosion with oxygen depolarization. Since the solubility of oxygen in aqueous media is low and its diffusion coefficient is much smaller than that of hydrogen ions, the rate of corrosion with oxygen depolarization is usually limited by diffusion. A typical polarization diagram for corrosion with oxygen depolarization is presented in a simplified form in Fig. 24.7. In this case the corrosion rate is equal to the limiting current for diffusion of oxygen to the surface of the corroding metal:

$$i_{cor} = {}_{O_2} i_d \qquad (24.20)$$

The rate of corrosion with oxygen depolarization is therefore almost independent (within certain limits) of the nature of the dissolving metal, in particular on its equilibrium potential and the anodic polarization. This can easily be seen from corrosion diagrams constructed for three dissimilar metals M, M_1 and M_2 (dot-and-dash lines in Fig. 24.7). Corrosion with oxygen depolarization may be accompanied by corrosion due to hydrogen evolution if the equilibrium potential of the hydrogen electrode in a given solution is more positive than that of the corroding metal (cf. dashed lines *1*, *2*, and *3* in Fig. 24.7). The limiting current is determined by the solubility of oxygen and by its diffusion coefficient, but it does not depend on the nature of the metal on which oxygen is reduced. As a result, the rate of corrosion with oxygen depolarization depends on the purity of the metal to a lesser extent than the rate of corrosion with hydrogen depolarization, and it varies more widely with the rate of agitation of the solution and the mode of oxygen transport to the metal.

24.6. METHODS OF CORROSION PROTECTION

Various methods of corrosion protection are used depending on the mode of corrosion and the conditions under which it occurs. The choice of the method is governed by its effectiveness in each particular case and also by economic factors. Any protective method alters the course of the corrosion process either by reducing its rate (corrosion inhibition) or by suppressing it completely. Polarization (corrosion) diagrams, which characterize the corrosion process most comprehensively, must also reflect changes in corrosion observed under the conditions of metal protection. These diagrams can therefore be used to work out possible ways for preventing metals from corrosion. They serve as a basis for ascertaining the specific features of protective methods. In considering existing methods of protection we shall use polarization diagrams in a somewhat simplified form (Fig. 24.8). On such diagrams, a linear relation between the current density and the potential of each partial reaction is postulated.

This simplification is justified in qualitative estimation of the peculiarities of most of the protective methods.

The effectiveness of protection is expressed by the inhibition coefficient γ or the degree of protection Z. The inhibition coefficient

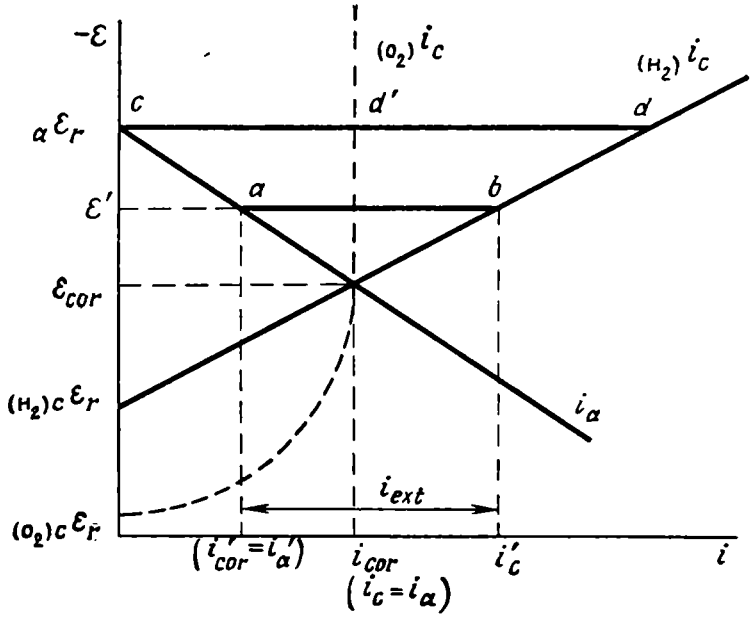

Fig. 24.8. Simplified polarization diagram for corrosion with hydrogen depolarization

indicates the total decrease in the corrosion rate achieved by the method used:

$$\gamma = \frac{i_{cor}}{i'_{cor}} \tag{24.21}$$

where i_{cor} and i'_{cor} are the rates of corrosion before and after protection. The degree of protection indicates to what extent the corrosion is suppressed by the method used:

$$Z = \frac{i_{cor} - i'_{cor}}{i_{cor}} \tag{24.22}$$

or

$$Z = \frac{i_{cor} - i'_{cor}}{i_{cor}} \text{ 100 per cent} \tag{24.23}$$

All methods of corrosion protection are divided into four groups

1. Electrical methods.
2. Methods based on changing the properties of a corroding metal.
3. Methods based on changing the properties of a corrosive medium.
4. Combination methods.

Electrical methods of corrosion protection are based on modifying the electrochemical properties of a metal under the influence of a polarizing current. The protection of metals against corrosion by imposing a cathodic polarization is most widely used. When the potential of a metal is moved to more electronegative values (with respect to the stationary corrosion potential), the rate of the cathodic reaction increases, and that of the anodic reaction falls (see Fig. 24.8). At the corrosion potential ε_{cor} the equality

$$i_a = i_c$$

was fulfilled; at a more negative value ε' this equality holds no longer:

$$i'_a \neq i'_c$$

i'_c being greater than i'_a.

The decrease in the rate of the anodic reaction upon cathodic polarization is equivalent to the decrease of the corrosion rate. The inhibition coefficient at the potential chosen ε' (see Fig. 24.8) will be equal to 2:

$$\gamma = \frac{i_{cor}}{i'_{cor}} = \frac{i_{cor}}{i'_a} = \frac{i_{cor}}{0.5 i_{cor}} = 2$$

and the degree of protection reaches 50 per cent:

$$Z = \frac{i_{cor} - i'_{cor}}{i_{cor}} \times 100 = \frac{i_{cor} - i'_a}{i_{cor}} \times 100 = \frac{i_{cor} - 0.5 i_{cor}}{i_{cor}} \times 100 = 50 \text{ per cent}$$

The external current i_{ext} required to move the potential to the value ε' is the difference between the cathodic and anodic currents:

$$i_{ext} = i'_c - i'_a$$

(its value in Fig. 24.8 is expressed by line *ab*). As the external current rises the potential is moved to more negative values and the corrosion rate must fall continuously. When the potential of the corroding metal becomes equal to the equilibrium potential of the anodic process ${}_a\varepsilon_r$, the rate of corrosion becomes equal to zero ($i_{cor} = i_a = 0$), the inhibition coefficient to infinity, and the degree of protection to 100 per cent. The current density that has to be provided to achieve full cathodic protection is called the protection current i_p. Its value in Fig. 24.8 is represented by section *cd*. The protection current is independent of the specific features of a given anodic reaction, in particular, of the magnitude of the polarization accompanying this reaction; it is completely determined by the cathodic polarization curve. For example, in changing from hydrogen to oxygen depolarization the protection current falls and becomes equal to the diffusion limiting current (line *cd'* in Fig. 24.8).

The protection of metals by cathodic polarization is used to increase the stability of underground and underwater metal structures and also of structures in contact with agressive chemical media.

It is economically justified in those cases where the corrosive medium possesses a high electrical conductivity and the voltage drop (associated with the flow of the protection current) and, hence, the power consumption are relatively low. The cathodic polarization of the metal to be protected is achieved either by imposing a current from an external source (cathodic protection) or by setting up a macrogalvanic couple with a less noble metal (usually, aluminium, manganese, zinc or their alloys). This auxiliary metal acts as the anode and dissolves at a rate sufficient to produce the required current in the system. An auxiliary metal which is made to dissolve (corrode) in place of the metal to be protected is often called the sacrificial anode.

A method of protection of metals against corrosion has recently been developed, which is based on imposing anodic polarization. This method is applicable only to metals and alloys capable of passivation when their potential is shifted in the positive direction, i.e., to metals whose anodic polarization curve is similar to the one given in Fig. 23.3. When the passive-state region is attained, the rate of dissolution of the metal may fall abruptly and become lower than its rate of self-dissolution in the absence of external polarization.

Electrical methods of corrosion protection also include so-called electrical drainage used to protect buried metal structures against the destructive effect of stray currents. In this method, anodic areas which cause corrosion are detected on a buried metal structure and connected by metallic conductors to sources of stray currents (e.g. tramway rails, d-c cables). All the current will then flow through the metallic conductor and the danger of an anodic reaction will be eliminated.

The protection of metals based on altering their properties is achieved by special treatment of their surface or by alloying.

The treatment of the surface of a metal to decrease its corrosion is carried out by any one of the following methods: (1) coating a metal with surface passivating films of its sparingly soluble compounds (oxides, phosphates, sulphates, tungstates used separately or in combination); (2) covering the metal surface with protective coats of oils, greases, bitumens, paints, enamels, etc.; and (3) applying coatings of other metals which are more stable under given conditions than the metal to be protected (tinning, plating with zinc, copper, nickel, chromium, lead, rhodium, etc.).

The protective action of most of the surface films is achieved by mechanical separation of the metal from its corrosive environment. According to the local-cell theory, their effect is due to the increase of electrical resistance (Fig. 24.9*a*). From the standpoint of the kinetic theory of corrosion it should be ascribed to the setting up of an additional energy barrier, which increases the polarization of the anodic and cathodic processes (Fig. 24.9*b*).

The increased stability of iron and steel articles coated with other metals is due to mechanical isolation of the surface and to the alteration of its electrochemical properties. In this mode of protection the reversible potential for the anodic reaction is shifted to more positive values (coating with copper, nickel, rhodium) or the polarization of the cathodic reaction is increased, i.e., the hydrogen overpotential is raised (zinc, tin, lead). As follows from the diagrams of Fig. 24.5 and also from Eq. (24.18) all these changes reduce the rate of corrosion.

The surface treatment of metals is aimed at preventing corrosion of machines, equipment, apparatus and household articles during

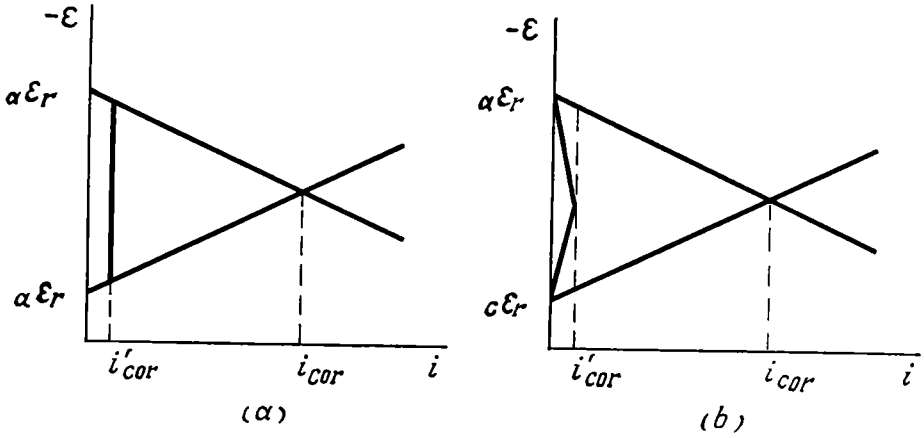

Fig. 24.9. The decrease of the corrosion rate in the presence of a protective surface layer due to increased ohmic resistance (*a*) and increased energy barrier (*b*)

transportation and storage (oils, greases, passivating films) and at long-term protection in service (varnishes, paints, enamels, metallic coatings). A common drawback of these methods is that when the surface layer wears out or is damaged the intensity of corrosion may sharply increase, and a new coating sometimes cannot be applied. In this respect alloying is considerably more effective in increasing the corrosion resistance of metals, although it is usually more expensive. An example is the alloying of copper with gold. To protect copper reliably against corrosion it is necessary to add to it a considerable amount of gold (not less than 52.5 at.%). Gold atoms mechanically protect copper atoms from interaction with the environment. Incomparably less alloying component is needed to increase the stability of the metal if this component is capable of combining with oxygen to form a protective passivating film. For example, the addition of several per cent of chromium sharply enhances the anticorrosive stability of steels. Of theoretical and practical interest is the increase of the corrosion resistance of metals by alloying them with cathodic additives (Tomashov). To elucidate

the principles on which this method is based, we will consider potentiostatic curves after Kolotyrkin. In the absence of externally applied polarizing current a metal is at a stationary potential ε_{cor} (Fig. 24.10) lying in the region of its active dissolution (before alloying). The rate of corrosion is determined here by the point of intersection of the $\overleftarrow{i}_M$ and $_{(1)}\overrightarrow{i}_H$ curves and corresponds to the current i_{cor}. Upon addition of a small amount of palladium (or

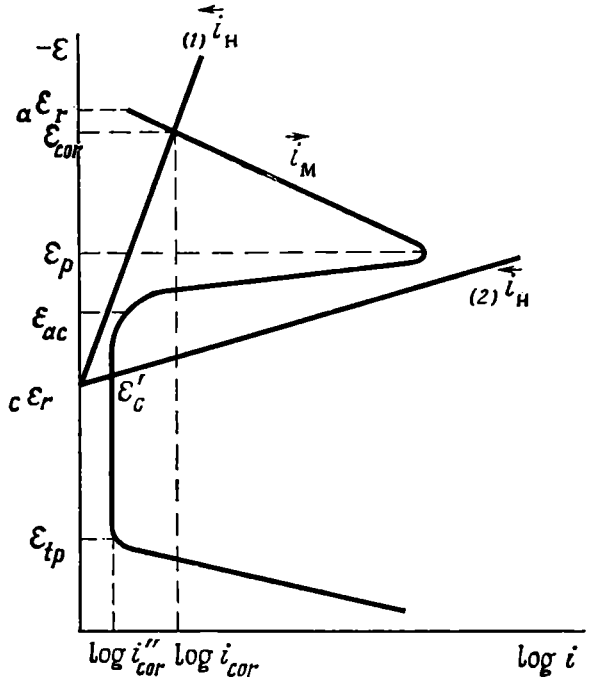

Fig. 24.10. Polarization diagram showing the possibility of protecting a metal against corrosion by increasing the rate of the cathodic process and shifting the steady-state potential to the passivity region

any other metal of low hydrogen overpotential) to the parent metal the polarization curve for hydrogen evolution will correspond to the straight line $_{(2)}\overrightarrow{i}_H$, which intersects the anodic curve already in the passivity region. As a result, the stationary corrosion potential is shifted to the positive side up to a certain value ε'_{cor} and the corrosion rate drops down to i'_{cor}, which corresponds to the rate of dissolution of the metal in the passive state. Thus, the corrosion rate is reduced here by decreased retardation of the cathodic process. Such a mechanism of corrosion protection is possible only where the reversible potential of the hydrogen electrode is more positive under the given conditions than the Flade potential and the point of intersection of the cathodic and anodic polarization curves lies in the region of the passive state of the metal (Fig. 24.10).

The corrosion rate can also be decreased by altering the properties of the corrosive medium. This is achieved either by special treatment of the medium with a view to depress its aggressiveness or by introducing into it small amounts of special substances, so-called corrosion inhibitors.

The treatment of the corrosive medium is carried out by any methods which lower the concentrations of its aggressive constituents. For example, in neutral salt solutions and in fresh water one of the most aggressive components is oxygen. It is removed by deaeration (boiling, distillation, bubbling with an inert gas) or by binding it with appropriate reagents (sulphates, hydrazine, etc.). The lowering of the oxygen concentration diminishes almost linearly its reduction limiting current and hence (see Fig. 24.7) the rate of corrosion of the metal. The aggressiveness of the medium can also be depressed by alkalization, decreasing the total content of salts and replacing more aggressive ions with less aggressive ones. In the anticorrosive treatment of water aimed at depressing its scale-forming tendency it is very often purified with ion-exchange resins.

Corrosion inhibitors are classified as liquid-phase and vapour-phase or volatile, depending on the conditions of their use. Liquid-phase corrosion inhibitors are subdivided according to their utilization (in neutral, alkaline or acidic media). The inhibitors most often used for neutral solutions are inorganic compounds of the anionic type. Their inhibiting effect is evidently associated either with the oxidation of the metal surface (nitrites, chromates) or with the formation of a film of a difficultly soluble compound between the metal, the given anion and, possibly, oxygen (phosphates, hydrophosphates). An exception is benzoates, whose inhibiting effect is mainly associated with adsorption phenomena. All corrosion inhibitors used for neutral solutions slow down predominantly the anodic reaction, causing a shift of the stationary potential in the positive direction (see Fig. 24.5). No effective corrosion inhibitors have been found so far for protection of metals in alkaline solutions. Only high-molecular-weight compounds possess some inhibitive properties.

Corrosion inhibitors for acidic solutions are almost exclusively organic substances containing nitrogen, sulphur or oxygen in the form of amino, imino, and thio groups and also as carboxyl, carbonyl and some other groups. It is commonly held that the inhibiting action of organic substances is due to their adsorption at the metal-acid interface which retards cathodic and anodic reactions, thereby reducing the corrosion rate. In connection with the predominantly adsorptive effect of organic inhibitors of acid corrosion the magnitude of the surface charge of the corroding metal, i.e., the value of its φ potential, is of special importance for understanding the mechanism of their inhibiting action and for a rational approach to the deve-

lopment of new inhibitors. The application of the correlative scale of potentials allows one to use data of electrocapillary measurements on mercury in solutions containing organic substances in order to estimate their efficiency as corrosion inhibitors for iron and other metals in contact with acidic media. Knowing the φ potential of the metal subjected to corrosion, one can calculate the inhibition coefficients as well as predict which substances will act as corrosion inhibitors. Experimental values of the inhibition coefficients

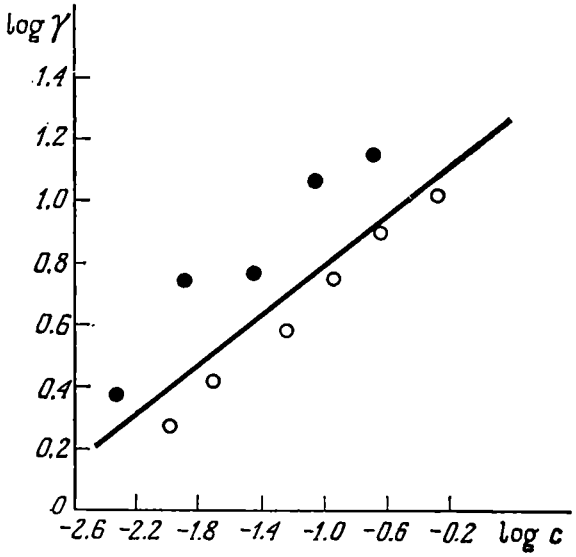

Fig. 24.11. Comparing experimental and calculated (straight line) coefficients of inhibition of the acid corrosion of iron on addition of different amounts of diethylamine. Filled and empty circles represent experimental data obtained by different authors

for retarding the corrosion of iron in acidic media in the presence of different amounts of diethylamine are given in Fig. 24.11 along with the theoretical straight line plotted according to the equation

$$\log \gamma = \text{const}_S + \text{const}_\sigma + \beta_\sigma \log c \qquad (24.24)$$

where const_S is a quantity constant for any member of the homologous series of amines and pyridines, and const_σ and β_σ are found from electrocapillary measurements on mercury.[1)]

However, adsorption is only a necessary precondition for the manifestation of the inhibiting effect of organic substances, and it does not determine completely the actual effect of inhibitors. This actual effect depends also on many other factors, viz. the electrochemical characteristics of a particular corrosion process, the nature

[1)] Const_σ corresponds to the surface-tension decrement $\Delta\sigma$ at a concentration of the inhibitor c equal to 1 mole/litre, and β_σ, to the slope of the straight line in the equation $\log \Delta\sigma = \text{const}_\sigma + \beta_\sigma \log c$.

of the cathodic reaction, the magnitude and nature of hydrogen overpotential (in corrosion with hydrogen depolarization), possible chemical transformations of inhibitors during corrosion, etc. In certain cases the effects of these factors may prevail, in which case simple relations like Eq. (24.24) cease to operate. But even then they are useful because they allow one to judge the mechanism of inhibition on the basis of deviations observed.

The effect of most of corrosion inhibitors used in acidic media is reinforced by the addition of surface-active anions: halides, sulphides and rhodanides.

Vapour-phase inhibitors are used for corrosion protection of machines, apparatus and other metal articles during their service in the air medium, during transportation and storage. Vapour-phase inhibitors are sprinkled as a solid in a container or packing case, or placed in a muslin bag close to the surfaces to be protected. Owing to the sufficiently high vapour pressure volatile inhibitors reach the metal-air interface and dissolve in the moisture film covering the metal. Then they are adsorbed from the solution on the metal surface. The inhibiting effects in this case are similar to those observed with liquid-phase inhibitors. The compounds commonly used as vapour-phase inhibitors are amines of low molecular weight to which corresponding groups (e.g. NO_2 or CO_2) are added. In connection with the specific conditions of their use the toxicity of vapour-phase inhibitors should be kept to a minimum.

To protect metals against corrosion, combination methods are often used. For example, to prolong the service life of underground pipelines, mechanical means of corrosion protection (insulating materials, bitumen compositions, etc.) are used in combination with cathodic protection, which prevents the metal from corrosion at spots unprotected by the insulating layer. Paints used to prevent metals from corrosion contain a corrosion inhibitor; thus mechanical protection is combined with electrochemical protection. The imposition of cathodic polarization enhances the retarding effect of inhibitors in neutral and acidic media. In the first case the effectiveness of corrosion protection is increased mainly by alkalizing the solution near the metal surface, which facilitates the formation of difficultly soluble compounds. In acid media an increase in the efficiency of protection results from the increase in the adsorbability of organic cations when the potential of the metal is shifted in the negative direction, i.e., when its negative charge is increased. Some organic substances which do not affect the corrosion of iron in neutral media become efficient inhibitors when the cathodic polarization is applied.

The net effect of combined protective methods is usually higher than the separate effect of the corresponding individual methods.

CHAPTER 25

Some Problems of Modern Electrochemistry

Present-day electrochemistry has not only solved many old problems of classical electrochemistry but also formulated new problems and developed novel trends called forth by the general progress of science and technology.

Mention should primarily be made of such new trends as the electrochemistry of semiconductors, chemotronics, and fuel cells.

Semiconductor electrochemistry as a new branch of theoretical electrochemistry owes its origin to two main factors. First, many electrochemical processes taking place at the electrode-electrolyte interface actually occur on a surface exhibiting the properties of semiconductors and having all the intrinsic features of this type of material. The conductivity of these surface layers—metal oxides and hydrides, intermetallic compounds, etc.—lies between the conductivities of metals and dielectrics. It is sensitive to the presence of traces of impurities and increases with temperature, in contrast to the conductivity of metals. The passage of a current through semiconductors is accomplished, in a general case, by electrons (n-type conductivity) or by holes, i.e., vacancies left after electrons have moved to another energy band (p-type conductivity). In contrast to metals, in semiconductors there is a wide space-charge layer near their contact with other phases, which complicates the picture of the electric double layer. Interpretation of the kinetics of many electrochemical reactions (processes in chemical sources of electricity, anodic dissolution of metals, etc.) is therefore impossible without elaboration of the electrochemistry of semiconductors. Second, an important role in the technology of production of semiconducting materials used to fabricate electronic devices, solar batteries, etc., is played by processes which are electrochemical in nature. Among these processes are the anodic and ordinary etching of semiconductors, the deposition of thin layers of a metal on the surface of semiconductors, etc.

Chemotronics, which has emerged only recently, is concerned with electrochemical systems capable of functioning as individual components and even assemblies in intricate electronic and cybernetic circuits. Relatively simple electrochemical cells (and their combinations) can be used as diodes, pressure pickups, integrators, multi-

pliers, memory devices, etc. The specific feature of chemotronic devices is that they are most convenient for measurements and control of processes involving comparatively low frequencies (usually below 1000 Hertz) at which electronic and semiconductor devices are almost inapplicable. This feature of chemotronics arises from the fact that, in distinction to radio valves and semiconductors, in which the electrons and holes are charge carriers, in chemotronic devices this role is played by ions, i.e., particles having a considerably larger mass and interia and, therefore, moving at a lower velocity. Another specific feature of chemotronic devices is that the flux of charged particles can be controlled not only by imposing an electric field, as in radio valves and semiconductors, but also by mass transfer, i.e., changing the conditions of diffusion and convection. Thanks to this property chemotronic devices are more universal than electronic and semiconductor devices.

Still another feature of chemotronic devices is the nature of the medium in which charge carriers migrate. The medium presently used in chemotronic devices is a solution (usually aqueous) of a corresponding electrolyte (commonly potassium iodide with a small amount of iodine). In radio valves, the electrons move in a vacuum, and in semiconductors, in crystal lattice interstices. According to Lidorenko, who outlined the prospects of practical application of chemotronic devices, most diverse materials may be used as working media in chemotronic devices.

The third trend in the progress of electrochemistry is linked with the development of so-called fuel cells. This problem is of special topical importance and deserves a more detailed consideration.

A fuel cell (or an electrochemical energy producer) is an electrochemical device intended for direct conversion of chemical energy contained in the system "fuel + oxidant" into electrical energy.

At present, the most widespread method of utilizing the chemical energy of a fuel is to burn it up in steam boilers or in internal-combustion engines. Here the chemical energy of the fuel is transformed into the heat energy of the reaction products:

$$\text{fuel} + \text{oxygen} = \text{reaction products} + (\text{heat energy})$$

Since the ultimate purpose of operation of any engine is to perform some work, the transformation of chemical energy into heat is followed by the conversion of this heat into mechanical energy and then, if required, into electrical energy. Thus, the following energy-conversion cycle is accomplished:

$$\text{chemical energy} \xrightarrow{\text{I}} \text{heat} \xrightarrow{\text{II}} \text{mechanical energy} \xrightarrow{\text{III}} \text{electrical energy}$$

All the three stages of energy conversion involve losses. However, while at stages I and III these losses may in principle be reduced

to a negligible value (depending merely on the perfection of the design), stage II involves losses which cannot be avoided by any improvement of the engine design. The reason lies in the specific nature of heat as a form of energy.

Heat is the energy of chaotically moving molecules. The transformation of heat into the energy of oriented movement of macroscopic bodies (mechanical energy) or into the energy of an oriented flux of charged particles (electrical energy) is possible only if there are two heat reservoirs: a source at a higher temperature T_2 and a sink at a lower temperature T_1. The degree of conversion of heat $\overline{Q}$ into work A depends on the ratio of these temperatures and cannot, even under the most favourable conditions, exceed the value defined by Carnot's theorem:

$$\frac{A}{\overline{Q}} \leqslant \left(1 - \frac{T_1}{T_2}\right) \tag{25.1}$$

In practice, the efficiency of steam engines is 4-8 per cent, that of powerful heat-and-power stations up to 30 per cent, and of powerful stationary internal-combustion engines from 40 to 50 per cent. Thus, in present-day heat engines 50 to 95 per cent of the original chemical energy of a fuel is wasted, the greater part of these efficiency losses being unavoidable.

In contrast to heat engines, in fuel cells the chemical energy is directly converted into electrical energy without an intermediate heat stage:

$$\text{chemical energy} \rightarrow \text{electrical energy}$$

Thus the limitations imposed by the second law of thermodynamics do not apply here, and theoretically an efficiency close to 100 per cent can be achieved.

In a fuel cell, the overall chemical reaction of fuel combustion

$$\text{fuel} + \text{oxidant} = \text{reaction products} + \overline{Q}$$

is split up into two interconnected partial electrochemical reactions taking place at electrodes and involving electrons:

(1) at anode: $\quad \text{fuel} = \text{fuel oxidation products} + ze$
(2) at cathode: $\quad \text{oxidant} + ze = \text{oxidant reduction products}$

When passing through the external circuit from the anode to the cathode the electrons can perform useful work. In other words, the chaotic movement of electrons between the reacting particles, accompanied by the evolution of heat (ordinary combustion), is replaced by an ordered transfer resulting in useful work (electrochemical combustion).

In a fuel cell, as in any other galvanic cell, the amount of energy that can be converted to work corresponds to the change of free

energy (or Gibbs free-energy change) in the reacting system:

$$A_{max} = zFE = -\Delta G \tag{25.2}$$

The total change of the chemical energy stored in the reacting system corresponds to the enthalpy (heat-content) change or to the thermal effect of the reaction

$$\bar{Q} = -\Delta H \tag{25.3}$$

The difference between ΔH and ΔG is called the bound energy of the system; when a galvanic cell is operating, this energy can be converted only to heat but not to work:

$$\Delta H - \Delta G = T\Delta S \tag{25.4}$$

The thermodynamic efficiency of a fuel cell is determined, as in the case of a heat engine, by the ratio of the work which can be obtained from the cell to the heat effect of the reaction.

$$\frac{zFE}{\bar{Q}} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \tag{25.5}$$

As can be seen from Eq. (25.5), the thermodynamic efficiency of a fuel cell depends on the magnitude and sign of the entropy change during the reaction. It is usually a small value and the efficiency is as a rule close to unity (to 100 per cent); it may be smaller or greater than unity. In the latter case not only the entire internal energy of the system ($-\Delta H$) is converted to useful work but also a certain amount of heat absorbed by the cell from the environment. Conversely, if $\Delta S < 0$, then the efficiency will be smaller than unity and the corresponding part of the thermal effect, equal to $T\Delta S$, is dissipated as heat.

If the reaction involves gaseous substances, their contribution to the total entropy is greatest since the gas state is the least ordered one. Accordingly, when gaseous substances are consumed in the course of the reaction the entropy of the system may be expected to decrease, and the theoretical efficiency will be smaller than unity; when gaseous substances are formed, the opposite effect is observed, i.e., the entropy of the system will increase and the efficiency will be greater than unity. For example, at room temperature the reaction of coal combustion

$$C + O_2 = CO_2$$

where the number of moles of gaseous substances does not change ($\Delta n = 0$), must have a theoretical efficiency nearly equal to unity with an emf of 1.02V. The reaction of incomplete combustion of coal ($\Delta n = +0.5$)

$$C + {}^1/_2O_2 = CO$$

under the same conditions gives, respectively, 1.25 and 0.7V. For a reaction in a hydrogen-oxygen fuel cell ($\Delta n = -1.5$)

$$H_2 + {}^1/_2O_2 = H_2O \text{ (liquid)}$$

one has 0.83 and 1.23V.

Technical data for some combustion reactions which can be used in fuel cells are listed in Table 25.1.

TABLE 25.1

Technical Data for Some Combustion Reactions

Reaction	z	Δn	300°K		900°K	
			E	Efficiency	E	Efficiency
$C + O_2 = CO_2$	4	0	1.02	1.00	1.02	1.02
$2C + O_2 = 2CO$	4	+1	0.70	1.25	0.98	1.75
$2CO + O_2 = 2CO_2$	4	−1	1.33	0.91	1.06	0.72
$CH_4 + 2O_2 = CO_2 + 2H_2O$	8	0	1.04	1.00	1.04	1.00
$H_2 + O_2 = 2H_2O$	4	−1	1.18	0.94	1.03	0.80

The practical efficiency of the existing fuel cells is much lower than theoretical (50-80 per cent), but greatly exceeds the efficiency of heat engines.

Thus, the foremost feature of fuel cells is the possibility of direct conversion of chemical energy into electrical at a high efficiency. It should be noted that this specific feature, as well as all the above thermodynamic regularities, refers not only to fuel cells but also to conventional chemical sources of electricity—galvanic cells and storage batteries. In these, as mentioned earlier, the chemical energy of active substances is also directly converted into electrical energy. Fuel cells differ from ordinary electrochemical energy producers in that the reactants (fuel and oxidant) are not incorporated into the electrodes beforehand, but are continuously fed to them during operation. This is the reason why fuel cells can operate continuously for an indefinite period of time while the reactants are supplied and the reaction products removed. Continuous operation is the second distinctive feature of fuel cells.

Fuel cells possess other, less unique features, owing to which they are preferred in a number of special fields of application. These include the absence of moving parts, constant readiness for operation, high effectiveness over a wide range of loads, silent operation and, for some types of fuel cells, the absence of harmful waste products.

A clearcut formulation of the advantages offered by the electrochemical burning-up of a fuel in comparison with ordinary chemical combustion reactions was first given by Yablochkov in the 1880's,

and at the same time he received his first patent for the invention of the fuel cell. Later the idea of the fuel cell was developed by Ostwald. However, attempts at constructing a fuel cell suitable for practical use faced considerable difficulties at the very outset due primarily to the electrochemical inertness of coal. Even at temperatures of the order of 1000°C the rate of the electrochemical burning-up of a solid fuel remains too low. Besides, a cell using a solid fuel soon becomes inoperative because of the accumulation of ash. Fuel cells in which a solid fuel is used indirectly as a reducing agent have proved somewhat more effective. In these cells, the electrochemically active substances are appropriately selected redox systems. For example, the following processes can be used:
at the negative electrode

$$Sn^{2+} \rightarrow Sn^{4+} + 2e$$

at the positive electrode

$$Br_2 + 2e \rightarrow 2Br^-$$

The tetravalent stannic ions formed are reduced externally by a primary fuel (coal) and the bromide ions are oxidized by atmospheric oxygen and then fed back to the cell to complete the cycle. Redox fuel cells, as they are called, have not yet found practical application, but work along these lines is in progress.

At present all attempts at using solid fuels in fuel cells have been abandoned and attention is mainly focused on the use of gaseous and liquid fuels, which exhibit a higher chemical activity and are technologically more convenient. The most promising liquid fuels are methyl and ethyl alcohols, formaldehyde, and hydrazine; efficient gaseous fuels include ethylene, butane, propane and other hydrocarbon gases, vapour-phase gasoline, carbon monoxide, and hydrogen. The oxidant is predominantly oxygen (pure oxygen or air), but other oxidants (e.g., hydrogen peroxide, chlorine and nitric acid) are also used for special purposes.

The development and construction of efficient fuel cells is a highly complicated engineering problem, and its solution has become possible only within the last 10-15 years due to the latest achievements in electrochemistry. Fuel cells have to meet a number of rather stringent and sometimes contradictory requirements. The basic requirement is to provide sufficiently high rates of electrode processes for a long period of time. To put it differently, the electrodes of a fuel cell must possess a high electrochemical activity, i.e., provide high current densities at low polarization. The second requirement refers to the electrolyte. It must possess a high ionic conductivity and stability, i.e., its composition must remain unchanged during its interaction with the fuel, oxidant or reaction products. At the same time the electrolyte should not cause corrosion of the electrode

or other parts of the cell. Fuel cells have to meet other requirements as well. They include a continuous and uniform supply of active substances to the working surfaces of the electrodes, removal of the reaction products from the cell, compactness and lightness of the construction, and a long service life.

This set of requirements is very difficult to meet and therefore only a few constructions of fuel cells suitable for practical use are known at present, though intensive research is being carried on in a number of countries.

The high electrochemical activity of electrodes of fuel cells is achieved by various methods: increase of the temperature, use of catalysts and of electrodes with a large surface area, etc. A considerable increase in temperature (up to 400-900°C and higher) is usually resorted to in cases where electrochemically inactive substances, e.g., hydrocarbon gases and carbon monoxide, are employed as fuels. A device working at such temperatures is called a *high-temperature fuel cell*; an important contribution to the development of this type of fuel cell was made by Davtyan (1946). The electrolytes used in high-temperature fuel cells are either molten carbonates (or metal hydroxides) or solid electrolytes possessing a sufficient ionic conductivity at high temperatures. The advantages of such fuel cells are the possibility of using low-activity and relatively contaminated fuels and the high intensity of the process. Their disadvantages are the difficulties associated with operation at high temperatures and with selecting stable materials, high consumption of energy for heating and compensation of heat losses.

There are fuel cells with aqueous electrolytes operating at slightly elevated temperatures (180-250°C) and a pressure of 5 to 50 atm. They are called *moderate-temperature fuel cells.* This category includes first of all the hydrogen-oxygen cell designed by Bacon, in which an alkaline electrolyte and porous nickel electrodes are used. Moderate-temperature fuel cells with concentrated phosphoric acid as the electrolyte may prove suitable for electrochemical burning of gaseous hydrocarbon fuels.

Much attention is focused at present on low-temperature fuel cells operating at temperatures up to 100°C. Such cells are simpler in design and considerably more convenient in operation than high- and moderate-temperature ones. The electrode processes in low-temperature cells are accelerated by using catalysts of maximal activity. However, since such catalysts are highly sensitive to contaminations, only sufficiently pure substances may be used as fuels and oxidants.

Present-day low-temperature hydrogen-oxygen fuel cells have a current density of up to 300 mA/cm^2 and a specific power of up to 200 W/kg. In fuel cells operating on a liquid fuel (alcohol) these characteristics are approximately one order of magnitude lower.

In low-temperature hydrogen-oxygen fuel cells so-called *gas-diffusion electrodes* are widely employed. These are porous metallic (most frequently nickel) plates consisting of two layers. One layer, in contact with the electrolyte, has small pores and faces the other electrode; this layer, called the *electrolyte retainer*, is backed up with another layer in contact with the gas phase and having larger pores (the *supporting* or *working layer*). This electrode structure, originally developed by Bacon, provides a large interface between the gas and the electrolyte and ensures their intimate contact. The interface is here in the immediate vicinity of the surface of the solid phase on which the electrochemical reaction takes place. The gas is prevented from bubbling through the electrode by the capillary pressure of the liquid contained in the small pores of the retaining layer. Thus a full utilization of the combustible gas and oxygen is achieved.

A catalyst is introduced into the supporting layer. The catalyst used for a hydrogen electrode is finely divided nickel (Raney nickel) produced by leaching aluminium out of its alloy with nickel. The remaining nickel has a distorted crystal lattice and a large surface area reaching 100 m^2/g. It is therefore a very active catalyst for the ionization of hydrogen. It was first used in the fuel cells invented by Justi[1]. The oxygen electrode usually contains silver as an active ingredient, which serves as catalyst for decomposition of hydrogen peroxide, the primary product of the cathodic reduction of oxygen in the alkaline solution.

Porous electrodes are the scene of complex and interrelated processes, which may briefly be described as follows. The gas, penetrating through the liquid-free pores into the supporting layer of the electrode, dissolves in the electrolyte film covering the inner surface of the pores and then, diffusing through the film to the metal surface, is adsorbed on it. Then follows ionization of the adsorbed gas, i.e., the electrochemical process, which is accompanied by the generation of electricity. The products of the electrode reaction diffuse through the electrolyte film from the supporting layer into the space between the electrodes.

The directly measured electrochemical parameters of porous electrodes (their macrokinetic characteristics) are determined by the superposition of the processes described above, which are associated both with the nature of the elementary electrode reaction (microkinetics) and with the transfer of the substance and electricity inside the electrode pores (macrofactors). The interplay of the micro- and macrofactors results in the intensity of the discharge process being distributed unevenly over the inner surface of the porous electrode. The

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[1] Such astructure is sometimes called a *DSK* electrode because the inventor, Justi, used this abbreviation.—*Tr.*

highest intensity is usually observed on the electrolyte side of the electrode, to which the current passes easily through the liquid contained in the small pores. The intensity of the process gradually decreases in the bulk of the electrode. Therefore the efficient operation of gas-diffusion fuel cells requires not only the use of a highly active catalyst but also a rational choice of the porous structure of the electrode to ensure optimum conditions for supply of reactants to the inner surface.

Apart from porous nickel electrodes, carbon electrodes activated by small amounts of metals of the platinum group (e.g. Kordesh cells) are also used in some types of low-temperature fuel cells. In carbon electrodes, the necessary separation of the gas from the liquid in the bulk of the supporting layer is achieved by partial hydrophobization of the carbon material.

All hydrogen-oxygen (oxyhydrogen) fuel cells with a liquid electrolyte operate almost exclusively on alkaline solutions. These electrolytes have some shortcomings. First of all, they are carbonized when the air is blown through them. Besides, even when no current is drawn from the cell, the potential of the positive electrode is found to be lower than the reversible potential of the oxygen electrode under given conditions. This is attributed to the fact that the reduction of oxygen in alkaline solutions may lead to the formation of hydrogen peroxide instead of water with the resulting decrease in the electrode potential and the number of electrons participating in the reaction. The electrode material must therefore be catalytically active with respect to the reaction of hydrogen-peroxide decomposition.

Acid electrolytes are free from these shortcomings, but their use requires electrode materials of sufficiently high corrosion resistance. The best results have so far been obtained by using acid fuel cells with ion-exchange membranes. In fuel cells of this type the electrodes are made of silver gauze (for the oxygen electrode) and of platinum or palladium gauze (for the hydrogen electrode), and the electrolyte is a thin film of an ion-exchange resin, in which the current is carried practically by a single species of ions.

The development of fuel cells is closely linked with the problem of utilization of the chemical energy of by-products from chemical and electrochemical processes for generating electricity. For example, electrical energy can be obtained through decomposition of sodium amalgam, which is an intermediate in the mercury method of producing chlorine and caustic soda. A number of other chemical transformations can also be effected in principle via electrochemical processes to produce electricity as a by-product.

And, finally, fuel cells might be used in the future in combination with biochemical agents for rational utilization of organic waste and also of marine flora and fauna cast in tremendous amounts onto

sea and ocean shores. In such biochemical fuel cells, the organic substrate is oxidized with the aid of enzymes or corresponding microorganisms. A number of such substances have already been found. It has been established that they may produce either direct or indirect effect. In the direct mechanism the fuel and enzymes (or corresponding microorganisms) are to be in direct contact with the negative pole of the fuel cell. In the case of the indirect mechanism the effect of bacteria consists in splitting off hydrogen, which is then supplied to the electrode and is oxidized to produce water. Bacteria capable of functioning in biochemical fuel cells include, for example, *Pseudomonas methanica*. For their vital activity these bacteria make use of the carbon from methane or methyl alcohol with the simultaneous liberation of hydrogen. In the presence of these microorganisms either direct or indirect activation of the organic fuel is possible. A somewhat higher potential is produced in the first case, evidently due to the evolution of atomic hydrogen.

Properly organized large-scale research and engineering work on the development of efficient fuel cells carried on in many countries creates the necessary prerequisites for their utilization in the various branches of technology. The principal field of application of fuel cells at present is the power supply of communication systems and airborne equipment (in spacecraft). It may be expected that fuel cells will find wide use as a source of power in transportation (electric automobiles, electric locomotives, and other means of transportation which do not contaminate the atmosphere with harmful combustion gases), for the storage of energy from wind-driven generators, etc. The application of fuel cells instead of turbogenerators at large electric stations is now considered hypothetical because of their low efficiency when conventional fuels are used and because of the short service life of the existing fuel cells.

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